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# JOURNAL

OF

## THE CHEMICAL SOCIETY.

CONTAINING

THE PAPERS READ BEFORE THE SOCIETY,

AND

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN OTHER JOURNALS.

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# ERRATA.

The asterisk in the second column indicates that the line is counted from the bottom.

Page.	Line.	Error.	Correction.
59	13*	the Jura .....	the Franconian Jurassic formation.
60	2	valleys of the Jura .....	valleys of Franconia.
63	16	benzoic .....	benzoïn.
76	4*	VI .....	VII.
77	8, 9	isomeric with that of Williams and that described by Schmitt	identical with that of Williams, and isomeric with that described by Schmitt.
145	17, 18	dinitro - paraoxybenzoic acid	dinitro-para-amidobenzoic acid, and the oxyacid derived from it is dinitro-paraoxybenzoic acid.
248	17	aniline .....	methylamine.
270	5	one part of the apatite ...	one part of phosphate of lime in the form of apatite.
295	19*	which facts indicate .... $C_{24}H_{18}N_2$ as the formula of acridine	which facts would seem to indicate $C_{24}H_{18}N_2$ as the formula of acridine, but the vapour-density shows it to be $C_{12}H_9N$ .
300	4*	$\begin{matrix} CH_3 \\ CH_3 \end{matrix} \left. \vphantom{\begin{matrix} CH_3 \\ CH_3 \end{matrix}} \right\} CH-CH_2-CH_2- \\ CH_2-CH_2-CH_2OH$	$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2OH.$
337	18	Paternò .....	Patera.
435	2*	$\begin{matrix} C_2H_5 \\ C_4H_5 \end{matrix} \left. \vphantom{\begin{matrix} C_2H_5 \\ C_4H_5 \end{matrix}} \right\} O$ .....	$\begin{matrix} C_2H_5 \\ C_4H_7 \end{matrix} \left. \vphantom{\begin{matrix} C_2H_5 \\ C_4H_7 \end{matrix}} \right\} O.$
621	24	is agitated .....	is acidulated with hydrochloric acid and agitated.
718	9	all strongly .....	but slightly.
780	2	} xxiv .....	lxxiv.
788	14		
813	18*		
826	13		
781	2*	temperature .....	freezing temperature.
985	15	(? ethoxyl) .....	dele.
996	16	trichloride .....	pentachloride.
1004	14	J. T. Walker .....	J. F. Walker.
1030	19	exactly .....	dele.
1087	6, 23	butylene .....	rutylene.
1109	15	moister .....	drier.
1111	last	18·25 .....	5·37.
1138	8*	lb. ....	of its.





# JOURNAL

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## THE CHEMICAL SOCIETY.

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PAPERS READ BEFORE THE CHEMICAL SOCIETY.

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### I.—*On Essential Oils.* Part II.

By J. H. GLADSTONE, Ph.D., F.R.S.

EIGHT years ago I communicated a paper on Essential Oils to the Chemical Society, and in concluding it I promised a further communication, with experiments on the oxidised oils, and a fuller account of the chemical and physical history of some of the hydrocarbons. Shortly after the paper was printed, a series of unforeseen events took me almost wholly away from my laboratory; other scientific enquiries then engrossed my thoughts; and so the research on these essential oils was long laid aside. Now, however, I will endeavour to fulfil my promise, though not to carry out my whole design.

Before entering on any new observations, I wish to refer to some criticisms on my paper which Mr. Daniel Hanbury kindly sent me. They relate to the plants from which the oils are derived; and, as I know little of the subject myself, I will just place his statements against those of Mr. Piesse, on whose authority each of the controverted names was given.

Oil of calamus is distilled, not from *Calamus aromaticus*, but from the rhizome of *Acorus Calamus*.

Indian geranium oil is yielded by *Andropogon Pachnodes*.

The wild thyme of our heaths, *Thymus Serpyllum*, gives an essential oil, but the oil of thyme of commerce is from *Thymus vulgaris*.

During the past spring I was furnished by Mr. Piesse with specimens of some rare essential oils, not previously examined—those of citron, lign aloes, pimento, and vitivert.

The following were the determinations of the specific gravity and refraction of these oils as they came into my hands:—

Crude oils.	Specific gravity.	Temp. Cent.	Refractive indices.		
			A.	D.	H.
Citron .....	0·8914	10°	1·4729	1·4797	1·5011 ?
Lign aloes .....	0·8702	18°	1·4620	1·4679	
Pimento .....	1·0374	10°	1·5229	1·5325	1·5660 ?
Vitiver .....	1·0070	19·5°	1·5147	1·5218	

*Citron*.—This oil is obtained from the leaves of the lemon, *Citrus Limonum*. It was slightly yellow. It began to boil at 155° C., but the bulk consisted of a liquid having the boiling point 166°—168°; the specific gravity 0·8549 at 19·5°; the refractive index for A, 1·4680; and the dispersion 0·273. Its odour resembled that of lemon, and it was probably identical with the hydrocarbon found in other parts of the same plant.

*Lign Aloes*.—This is a colourless oil, with a characteristic pleasant odour, believed to be obtained from the wood of a large tree that grows in Mexico.\* The principal part distils over at somewhere about 200°, but it seemed impossible by fractional distillation, even with the aid of sodium, to obtain a body of a fixed boiling point. The specific gravity and optical properties of the best rectified oil are given later on in this paper; they will be found to resemble closely the properties of citronellol, suggesting the idea that the principal constituent may also have the composition  $C_{10}H_{16}O$ .

*Pimento*.—This pungent oil is derived from the seeds of *Myrtus Pimenta*. It began to boil at about 197°, and the thermometer rose gradually to 242°, about which temperature the greater portion passed into the receiver. The first portion consists partly of an oil insoluble in potash; the second is wholly dissolved by an alkali. When rectified, though perhaps not quite pure, it was found to have the boiling point 243°; specific gravity at 12·5°, 1·0436; refractive index for A 1·5281; and dispersion about 0·416. Its odour was that of eugenic acid, and like that body it was freely soluble in potash, giving two salts, of which that which contains the larger proportion of acid will separate from a moderately strong solution in crystalline masses. As the physical properties mentioned above accord sufficiently well with those previously determined for eugenic acid,† there can scarcely be a doubt that oil of pimento is substantially the

\* The Lign aloes of the sacred Scriptures is supposed to be the *Aquilaria Agallochum* of Northern India.

† Phil. Trans., 1863, p. 317.



same as oil of cloves, while each contains a small proportion of a hydrocarbon, to which is due the difference of their odours.\*

*Vitiver.*—The crude oil was very viscid, of a dark brown colour, with an odour suggesting both santal wood and patchouli. On repeated distillations it was found to consist mainly of a liquid boiling at  $280^{\circ}$ — $283^{\circ}$ , but the action of sodium showed that this was a mixture of two bodies, the one decomposable and the other unalterable by that metal. The rectified oils were of a brownish-green colour on being freshly distilled, and changed to a truer green shortly afterwards—a circumstance which I have not observed in any other case. An examination of the hydrocarbon is given below, and confirms the close resemblance of this oil to those of cedar and santal wood.

#### THE HYDROCARBONS.

These are all of the composition  $C_{10}H_{16}$ , or a multiple of that. In the previous paper I described several new ones, of which I analysed eight. No names were given them beyond that of the oil from which they were obtained, but now, in accordance with the usual practice, I would suggest the following:—

Hydrocarbon from Bay .....	Laurylene.
„ „ Calamus .....	Calamene.
„ „ Dill .....	Anethene.
„ „ Elder.....	Sambucene.
„ „ Eucalyptus amygdalina ..	Eucalyptene.
„ „ Myrtle .....	Myrtene.
„ „ Nutmeg .....	Myristicene.
„ „ Rosewood.....	Rhodiene.

#### *Polymeric Groups.*

When treating of the hydrocarbons of the essential oils in my previous paper, I distinguished between three polymeric groups, to which were assigned the formulæ  $C_{10}H_{16}$ ,  $C_{15}H_{24}$ , and  $C_{20}H_{32}$ . The first group was said to comprise the great mass of these hydrocarbons—turpentine, orange, caraway, nutmeg, anise, thyme, myrtle, and twenty others; the second, those derived from cloves, rosewood, cubebs, calamus, cascarilla, and patchouli; while the third group was represented by colophene.

That colophene also has its isomerides is rendered probable by the descriptions given of paracajputene, and of the substances from other

\* Since writing the above, I find the same conclusion had been previously arrived at by Oeser.

sources which have been named colophene, but which are probably not identical with it.

If there is this distinction, the vapour-densities of members of the three groups should be different. Now the densities of oil of turpentine, pepper, juniper, elemi, lemon, and orange, together with gaultherylene, valerene, citrene, terebene, carvene, and caoutchene had been determined by various experimenters to be about, though generally a little above, the theoretical density for  $C_{10}H_{16}$ , viz., 4.71. The experimental density of colophene given in Gmelin's Handbook exceeds what would be required by  $C_{20}H_{32}$ . No member of the second group, however, had been examined in this respect, unless it be cedrene, which appears to belong to it, and which gave, according to Walter, the vapour density 7.5.  $C_{15}H_{24}$  requires 7.06. I took the oils of patchouli and calamus.

	Calamene.	Patchouli.
Difference between weight of air } and vapour . . . . . }	·3327 grm.	·311 grm.
Temperature of balance case . . . . .	12.5° C.	9° C.
Temperature of sealing . . . . .	280° C.	294° C.
Capacity of globe . . . . .	110.8 c.c.	98.49 c.c.
Residual air . . . . .	2.6 c.c.	1.95 c.c.
Calculated density of vapour . . . . .	6.80	7.2

Each of these differs little from the theoretical 7.06, and they differ in opposite directions.

It is well known that several oils of the first group form compounds with hydrochloric acid of the composition  $C_{10}H_{16}.2HCl$ . It might therefore be anticipated that the oils of the second group would combine with a smaller quantity of hydrochloric acid; and indeed the hydrochloride of cubebene is said to be  $C_{15}H_{24}.2HCl$ . I tried patchouli and rhodiene. Dry hydrochloric acid gas was passed through the oil till it was perfectly saturated; in each case it remained liquid; portions were freed from excess of acid by exposure in vacuo over sticks of potash, or by heating in a water-bath, and analysed. Two different preparations from patchouli gave 7.11 and 11.18 per cent. of chlorine; the product from rhodiene purified in the two ways mentioned above gave 18.26 and 16.78 per cent. These numbers differ from one another, and from those deduced from any probable formula. They seem to indicate that these liquid hydrochlorides are somewhat indefinite.

The compound of colophene with the acid gas was similarly formed and examined. It was very viscid, and of a dirty brown rather than an indigo colour, as previously described. It lost nearly all this colour, together with the smell of hydrochloric acid, when heated in a water-bath or exposed over potash in vacuo; but it still retained some chlo-



rine, a very little however, for analysis showed only 1·76 per cent. in the first instance and 2·01 per cent. in the second. If we suppose the whole of the colophene combined with this hydrochloric acid we should arrive at the very improbable formula of nothing less than  $C_{120}H_{192}HCl$ . The power of  $HCl$  to combine with these hydrocarbons evidently becomes greatly diminished as their molecules become more complex.

The hydrocarbons of the first group, derived from oil of turpentine, orange-peel, cedrat, and thyme were found to require from 5·3 to 5·6 volumes of slightly diluted methylated spirit to dissolve them; while the hydrocarbons of the second group, from oils of calamus, cubebs, patchouli, and rosewood, required from 27 to 30 volumes. Colophene and paracajputene are almost, if not wholly, insoluble in aqueous alcohol.

It is well known that strong sulphuric acid acts powerfully on oil of turpentine, giving rise to two new isomeric compounds, terebene and colophene. It was found to have a similar action on the hydrocarbon from nutmeg; but when a member of the second group was submitted to its action, nothing analogous to colophene was produced.

Another distinction between the groups is a small but clearly recognizable difference in their expansibility by heat. On referring to my former paper it will be seen that the "sensitiveness" of the first group varies from 46 to 49, while that of the second group never exceeds 45, and averages 43. Colophene is only 41. In connection with this matter the following determinations were made of the expansion of oil of turpentine by heat:—

*Oil of Turpentine.*

Temperature.	Specific gravity.	Expansion for 5° C.
15° C.....	0·8665	—
20° .....	0·8632	0·0033
25° .....	0·8599	0·0033
30° .....	0·8565	0·0034
35° .....	0·8531	0·0034
45° .....	0·8464	0·00335

Oil of rosewood was found to expand 0·00321 or 0·00325 for each 5° C. between 0° and 50°.

Thinking that the hydrocarbon from oil of cedar, for which Walter obtained a vapour-density of 7·5, and to which he assigned the composition  $C_{16}H_{26}$ , was probably a member of the second group, I prepared some and purified it, as recommended by him, by distillation from anhydrous phosphoric acid. The result was a liquid having the following properties:—

Specific gravity at 18° C. ....	0·9231
Refractive index for A .....	1·4964
Dispersion.....	0·0276
Boiling point .....	252° C,
Solubility in alcohol .....	Slight.

These all agree with the properties of other hydrocarbons of the formula  $C_{15}H_{24}$ , with which also the proportions of carbon and hydrogen found by Walter are sufficiently in accordance.

Hydrocarbons were also obtained from oil of santal wood and oil of vitivert, by destroying the oxidized constituent by means of sodium; but the yield was small. In each case the oil was sparingly soluble in alcohol and rather viscid. Other properties were as follows:—

	Santal.	Vitivert.
Specific gravity.....	0·9190	0·9332
Refractive index for A.....	1·4867	1·5061
Boiling point.....	—	255° C.

This is enough to show the analogy to cedrene, but neither specimen was perhaps completely purified.

The general result of these observations, together with those previously made, will be seen by the subjoined table, by which also it will be evident that the middle or fifteen-carbon group is intermediate in all its properties, and that these three groups do not pass by insensible gradations into one another, but are separated by strongly-marked divisions.

	10-Carbon group.	15-Carbon group.	Colophene.
Formula .....	$C_{10}H_{16}$ .	$C_{15}H_{24}$	$C_{20}H_{32}$
Vapour-density .....	4·7	7·1	—
Character of liquid .....	Limpid	Viscid	Very viscid.
Specific gravity, at 20° C. ....	0·846—0·880	0·904—0·927	0·939
Refractive index for A, at 20° C. ....	1·457—1·467	1·488—1·497	1·5084
Dispersion.....	About 0·027	About 0·029	0·031
Sensitiveness.....	About 48	About 43	41
Boiling point .....	160°—176°	249°—260°	315°
Action of sulphuric acid.....	Polymerizes	Doubtful	None.
Solubility in aqueous alcohol.....	Freely soluble	Sparingly sol.	Insoluble.
Combination with HCl .....	$C_{10}H_{16} \cdot 2HCl$ and $C_{10}H_{16} \cdot HCl$	$C_{15}H_{24} \cdot 2HCl$ and in smaller pro- portions.	Very small quantity.

There is no difference in specific refractive energy, and the various members of the ten and fifteen-carbon groups at least have powerful



odours, and rotate the plane of polarization strongly, sometimes in one sometimes in the other direction.

### OILS CONTAINING OXYGEN.

Many of the essential oils consist, as is well known, of a body containing oxygen, mixed usually with a hydrocarbon of the first or second group. This is sometimes a product of the direct oxidation of the hydrocarbon, and then is generally a feebly acid resin; but in most cases the relation between the two is not apparent. Few of these oils have hitherto been carefully studied. My attention has been confined almost exclusively to those neutral oils which contain only one atom of oxygen.

#### *Citronella.*

The oxidised oil of which citronella is principally composed was submitted to analysis. It was purified by repeated fractional distillation till the boiling point was nearly uniform. Combustions were made in the usual manner.

I. Substance boiling at  $202^{\circ}$ — $205^{\circ}$  C. Specific gravity at  $20^{\circ}$  C., 0.8749. 0.4288 grm. gave 1.2230 grm. of carbonic acid, and 0.4215 grm. of water.

II. Substance boiling at  $199^{\circ}$ — $202^{\circ}$  C. Specific gravity at  $20^{\circ}$  C., 0.8741. 0.396 grm. gave 1.1355 grm. of carbonic acid, and 0.386 grm. of water.

These numbers indicate the composition  $C_{10}H_{16}O$ .

	Experiment.		Calculated.
	I.	II.	
Carbon .....	77.78	78.19	78.94
Hydrogen .....	10.92	10.83	10.53
Oxygen (loss) .....	11.30	10.98	10.50
	100.00	100.00	100.00

This was verified by a determination of the vapour-density.

Difference between weight of air and vapour 0.2912 grm.  
 Temperature of balance case .....  $8^{\circ}$  C.  
 Temperature of sealing .....  $254^{\circ}$  C.  
 Capacity of globe ..... 110.8 c.c.  
 Residual air ..... 0.6 c.c.  
 Calculated density of vapour ..... 5.83.

The theoretical density should be 5·33, but there was a brown stain left in the globe.

I propose naming this oil citronellol, in accordance with the usual plan of adopting -ol as the termination of the names of bodies of this nature.

The oxygenised oil obtained from wormwood is said also to have the composition  $C_{10}H_{16}O$ , but its physical properties are very different, as will be seen by the subjoined table, in which I have called it *absinthol*, to distinguish it from the hydrocarbon.

Oil.	Specific gravity at 20° C.	Boiling point.	Refractive Index A, at 20° C.	Dispersion.	Sensitive-ness.	Specific refractive energy.	Circular polarisation.*
Citronellol, Penang ..	0·8742	200°	1·4563	0·0251	50	·5219	—
Do. Ceylon ..	0·875	200°	1·4594	0·0262	46	·5251	— 13
Absinthol .....	0·9267	217°	1·4543	0·0243	43	·4903	+ 134

The refraction equivalent of citronellol is therefore 79·3 or 79·8, instead of the theoretical 73·7, as deduced from the composition  $C_{10}H_{16}O$ , while the equivalent of absinthol is only 74·5. The discrepancy in the case of citronellol is about the same as is found throughout the great phenyl group, as shown in my paper in the Journal of this Society (year 1870, p. 147), and if the two oils are really isomeric, it suggests an interesting difference in their molecular constitution.

#### *Cajeput.*

The oil of cajeput of commerce is said to be obtained from the leaves of *Melaleuca Leucodendron*, but the same oxidised compound was evidently the principal constituent of the oils derived from the leaves of *Melaleuca ericifolia* and *Melaleuca linarifolia*, as well as of *Eucalyptus oleosa*, oils sent to this country from the colony of Victoria.

This compound, though containing oxygen, may be distilled unchanged from metallic sodium. In this way the oils were freed from other oxidised products, and the specimens thus obtained exhibited the following physical properties:—

\* As in the previous paper, the circular polarisation is given as actually measured in a tube ten inches long. It can, of course, be easily reduced to any scale that may be preferred.



Oil.	Specific gravity at 20° C.	Boiling point.	Refractive Index $A_D$ at 20° C.	Dispersion.	Sensitive-ness.	Circular polarisation.
Cajeput .....	0·9160	174°	1·4532	·0213	45	— 2°
<i>Melaleuca ericifolia</i> ....	0·8960	173°	1·4560	·0239	48	+ 30
<i>Melaleuca linarifolia</i> ....	0·8985	173°	1·4651	·0263	46	+ 11
<i>Eucalyptus oleosa</i> .....	0·9075	171°—176°	1·4563	·0227	44	+ 10

The composition of cajeputol is well known to be  $C_{10}H_{18}O$ ; the refraction-equivalent of the specimen examined was therefore 76·2, which accords with the theoretical equivalent 76·3.

### *Carvol and its Isomerides.*

In my previous paper it was stated that the oils of spearmint and nutmeg contain oxidised liquids which appear to be isomerides of carvol, the principle which gives its peculiar flavour to the oil of caraway. They were named respectively menthol and myristicol. These have been submitted to a fuller investigation, and it has been found that oil of dill also yields a substance isomeric, or perhaps identical, with ordinary carvol.

There are two ways in which these oxidised oils may be separated,—either by fractional distillation, which must always be an imperfect method, or by taking advantage of the fact that they form crystalline bodies with hydrosulphuric acid, which can be easily purified, and which yield the original oil when decomposed by an alkali. The oil from nutmeg, however, was found not to form such a compound.

The following are the physical properties of the substances above mentioned. Menthol I was prepared by fractional distillation. Menthol II was prepared from the hydrosulphuric compound.

Substance.	Boiling point.	Specific gravity at 20° C.	Refractive Index $A_D$ at 20° C.	Dispersion.	Sensitive-ness.	Refraction equivalent.	Circular polarisation.
Carvol .....	227°	0·9530	1·4886	0·0345	46	51·26	+ 145°
Dill carvol .....	—	0·9562	1·4891	0·0333	45	51·15	+ 108°
Menthol I. ....	225°	0·9515	1·4839	0·0326	44	50·86	— 103°
Menthol II.....	225°	0·9394	1·4791	0·0311	42	51·00	— 114°
Myristicol .....	224°	0·9466	1·4848	0·0312	46	51·21	+ 31°

*Dill Carvol.*—The oxidised oil obtained from dill has the same odour as that from caraway, an odour which can scarcely be confounded

with any other. Like carvol also it forms a crystalline compound when treated with sulphide of ammonium in alcohol. 0·527 grm. of these crystals oxidised by strong nitric acid, and treated with barium salt, gave 0·360 grm. of sulphate of barium.

This result agrees with what should be obtained from the known hydrosulphate of carvole ( $C_{10}H_{14}O$ ) $_2H_2S$ .

	Calculated.	Found.
Carbon. ....	71·86	—
Hydrogen .....	8·98	—
Oxygen .....	9·58	—
Sulphur .....	9·58	9·37
	<hr/> 100·00	<hr/> —

I am disposed, therefore, to regard this compound derived from dill as identical rather than isomeric with carvol.

*Menthol*.—This compound has the very characteristic odour of spearmint, totally different from that of carvol, and it retains the same odour when it has been reproduced from the hydrosulphate.

A combustion was made. 0·3945 grm. yielded 1·159 carbonic acid, and 0·3415 water. This agrees with the formula  $C_{10}H_{14}O$ .

	Calculated.	Found.
Carbon .....	80·00	80·10
Hydrogen .....	9·33	9·62
Oxygen .....	10·66	—
	<hr/> 100·00	

Two determinations of the vapour-density were made.

Difference between weight of air and vapour..	0·2425	0·2897 grm.
Temperature of balance case .....	12° C.	12° C.
Temperature of sealing .....	277° C.	259° C.
Capacity of globe .....	97·2 c.c.	115·3 c.c.
Residual air .....	2·6 c.c.	1·3 c.c.
Calculated density of vapour .....	5·98	5·94

These are both rather above the calculated density, namely, 5·29.

The hydrosulphate forms very readily, giving silky needle-shaped crystals of great beauty. 0·442 grm., oxidised by nitric acid, gave 0·306 of sulphate of barium. 0·2227 grm. oxidised by hydrate of potassium and chlorine gave 0·1605 grm. of sulphate of barium. These determinations give respectively 9·80 and 9·89 per cent. of sulphur, instead of 9·58.

As the composition of these crystals seemed to be the same as that



of the hydrosulphate of carvol, and yet they yield a different oil on treatment with alkali, their relative solubility in ether was examined. At 23° C. one part of the hydrosulphate from the three sources required the following amount of ether to dissolve it:—

From caraway . . . . .	226 parts.
„ dill . . . . .	279 „
„ spearmint . . . . .	216 „

*Myristicol*.—This oil has the characteristic smell of nutmeg, and, unlike the preceding oils, it does not form a crystalline compound with hydrosulphuric acid.

It was found very difficult to purify it by fractional distillation, indeed there was some reason to think that in the process of rectification it was subject to change. An ultimate analysis of portions boiling at somewhere about 220° C. yielded rather too much carbon and hydrogen for the formula  $C_{10}H_{14}O$ , suggesting the idea of its being still mixed with some amount of a hydrocarbon. The vapour-density was determined.

Difference between weight of air and vapour	0·2512 grm.
Temperature of balance case . . . . .	9° C.
Temperature of sealing . . . . .	259° C.
Capacity of globe . . . . .	99·8 c.c.
Residual air . . . . .	0·6 c.c.
Calculated density of vapour . . . . .	5·71

This shows at least that myristicol belongs to the  $C_{10}$ , and not the  $C_{15}$ , or any other group. It accords with theory better than the numbers obtained for menthol do; and the other physical properties resemble those of carvol and menthol so closely that there can be little doubt it is isomeric with them.

### *Cassia.*

The extremely refractive and dispersive properties of Oil of Cassia have long been known to physicists. They depend on a substance that is now recognised as hydride of cinnamyl  $C_9H_8O$ . A careful preparation of this was made by the sulphite of sodium process, and it gave the enormous refraction of 1·6045 for  $A$  at 11° C. As the specific gravity was 1·059, the refraction-equivalent of the oil was 75·3, being an excess of 17 over the equivalent calculated from its ultimate composition. This excess is greater than that of any other substance known to me, except anthracene, and may, perhaps, throw some light on the molecular constitution of the compound. This interesting question of the refraction equivalents of these hydrocarbons and oxidised

oils has already been referred to in a paper published in our Journal for May, 1870, and I shall probably some day revert to the subject.

*Other Oxidised Oils.*

In addition to the substances already described, there are several oxidised compounds which have been separated more or less perfectly, and have been examined in regard to their physical properties, though they have not been analysed.

Oxidized oil, from	Specific gravity.	Boiling point.	Refractive Index A.	Dispersion.	Sensitiveness.	Rotation
Rose .....	0·881	216°	1·4647	·0283	47	—
Indian geranium .....	0·884	—	1·4692	·0295	59	— 3
Atherosperma Moschatum.	1·0386	224°	1·5143	·0460	46	+ 10
Lign aloes .....	0·8640	200°	1·4601	·0280	—	—

## II.—COMMUNICATIONS FROM THE LABORATORY OF THE LONDON INSTITUTION.

### No. III.—*Observations on the Nitrochlorophenols.*

By HENRY E. ARMSTRONG.

THE following experiments were undertaken with the object of obtaining further evidence as to the mutual relations of the various nitrochlorophenols, and more especially of dinitrochlorophenol melting at 110°—111°, the preparation of which I have described in my previous communication, to its isomerides, and to the nitrodichlorophenols.

Aug. Faust\* has lately given an account of some experiments on the nitration of the chlorinated sulpho-acids obtained by saturating the product of the action of sulphuric acid on phenol with chlorine, the object of which seems to have been to ascertain whether, by the action of sulphuric acid, more than two isomeric sulpho-acids were formed.† His results seem to be completely confirmatory of those which I obtained when operating upon the pure potassium salts of the dichlorinated sulpho-acids, and are entirely opposed to the assumption that

\* Zeitschr. f. Chem. [2], vii, 538.

† According to Solommanoff (Zeitschr. f. Chem. [2], v, 294), no less than three are thus formed; Kekulé and others agree that only two are obtained.



more than two isomeric bodies are generated by the action of sulphuric acid on phenol. Faust has furthermore succeeded in chlorinating dinitrophenol, and also in obtaining from dinitrochlorophenol ( $110^{\circ}$ — $111^{\circ}$ ) by Griess's method a mononitrochlorophenol isomeric with that obtained by nitration of monochlorophenol, or by chlorination of mononitrophenol (volatile modification). I have, it would seem, gone over much the same ground, and am able to confirm Faust's observations in every particular. He also brings forward one other extremely important experiment, viz., the conversion of trinitrophenol into dinitrochlorophenol ( $110^{\circ}$ — $111^{\circ}$ ) by the action of hydrochloric acid on diazodinitrophenol from picramic acid.

### *Chlorination of Dinitrophenol.*

According to Laurent, chlorine has no action on this body. I, therefore, in order to facilitate the chlorination, mixed the pure dinitrophenol with about one-sixth of its weight of iodine, and exposed the mixture, heated to about  $120^{\circ}$  in an oil-bath, to the action of dry chlorine. Even under these circumstances the chlorination was very imperfect, 30 grm. dinitrophenol not being more than half converted into chloro-product after three hours' heating. More successful was the action in presence of antimony pentachloride: a moderately rapid current of dry chlorine was passed for little more than two hours into a mixture of 35 grm.  $C_6H_3(NO_2)_2OH$  with 15 grm.  $SbCl_5$  heated to  $120^{\circ}$ ; at the end of this time the chlorination was complete. The product was mixed with water, the nitro-body extracted with dilute ammonia, the ammonium derivative recrystallised and then decomposed by dilute acid. Pure dinitrochlorophenol, melting at  $110^{\circ}$ — $111^{\circ}$ , was thus obtained, agreeing in every respect with that obtained by nitration of dichlorophenolparasulphonic acid. The barium, calcium, and magnesium derivatives were also compared and found identical.

2908 grm. gave 190 grm.  $AgCl$ , equivalent to 16.16 per cent. chlorine;  $C_6H_2(NO_2)_2ClOH$  requires 16.25 per cent.

*Barium Derivative*  $(C_6H_2(NO_2)_2ClO)_2Ba + 9\frac{1}{2}aq.$ —Air dry this contained 23.5 per cent.  $OH_2$ ; calculated 23.01 per cent. Dried *in vacuo* it becomes brilliant orange-vermilion in colour, and parts with all but one molecule of its water of crystallisation; thus 1.1934 grm. exposed for about 10 days over sulphuric acid lost 20.5 per cent.  $OH_2$ , and on heating to  $140^{\circ}$ , experienced a further loss of 2.54 per cent.  $OH_2$ .

*Magnesium Derivative*  $(C_6H_2(NO_2)_2ClO)_2Mg + 7aq.$ —In two determinations the air dry substance lost 21.8 per cent.  $OH_2$ ; calculated 21.5 per cent.

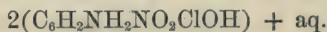
*Calcium Derivative*  $(C_6H_2(NO_2)_2ClO)_2Ca + 7aq.$ —The air-dry

substance was found to contain 21.13 per cent.  $\text{OH}_2$ ; calculated 20.96 per cent.

Chlorine appears to have no action on picric acid in the presence of antimony pentachloride.

*Amidonitrochlorophenol.*

Dinitrochlorophenol (melting point  $110^\circ$ — $111^\circ$ ) was dissolved in an excess of ammonia, and the warm solution saturated with hydrogen sulphide, filtered from separated sulphur, and allowed to cool; a deep red ammonium salt crystallised out. This was recrystallised, and then decomposed by acetic acid. The amido-product was filtered off and recrystallised from much hot water after digesting with a small quantity of animal charcoal. It then separates from the hot solution on cooling in long, fine, brass-yellow needles; these contain water of crystallisation, which they lose at  $100^\circ$ , and melt at about  $140^\circ$ .



·9196 air dry substance lost on drying at  $100^\circ$  ·0441 grm.  $\text{OH}_2$ .

·277 thus dried gave ·206 grm.  $\text{AgCl}$  and ·0004 grm.  $\text{Aq.}$

	Theory.	I.
$\frac{1}{2}\text{OH}_2$	4.55	4.79
Cl	18.83	18.84

Faust does not describe this body, but has prepared its hydrochloride, sulphate, and barium derivative.

*Chlorination of Orthonitrophenol.*

It was my intention to reduce dinitrochlorophenol ( $110^\circ$ — $111^\circ$ ) to nitrochlorophenol, and finally to monochlorophenol; but I wished before doing so, to obtain the hitherto undescribed monochloro-derivative of orthonitrophenol, inasmuch as I expected this would be identical with the reduction-product from this dinitrochlorophenol.

Chlorine was passed into a flask containing a weighed quantity of orthonitrophenol melted under water until the calculated increase of weight was obtained. The product is somewhat difficult of purification; best by conversion into ammonium derivative, and repeated recrystallisation of the latter. On decomposing this with dilute acid the phenol separates out in beautiful silky white needles, usually grouped in tufts. These are soluble to a considerable extent in hot water. It readily fuses to an oil under water, and melts in the dry state at  $109^\circ$ — $110^\circ$ . Faust's description of his reduction-product from dinitrochlorophenol ( $111^\circ$ ), and of its metallic derivatives, agrees

perfectly with the above body, and I doubt not the two are identical. He states, however, that it melts at  $111^{\circ}$ , viz., at the same temperature as the dinitrochlorophenol, from which it is obtained.

·2456 grm. gave ·2033 grm. AgCl, equivalent to 20·81 per cent. chlorine;  $C_6H_3NO_2ClOH$  requires 20·46 per cent.

*Potassium Derivative*,  $C_6H_3NO_2ClOK + aq.$ —Brown-yellow tufts of needles, very soluble in water.

·7185 grm. lost at  $140^{\circ}$  ·0528 grm.  $OH_2$ , equivalent to 7·34 per cent.; calculated 7·84 per cent.

*Barium Derivative*  $(C_6H_3NO_2ClO)_2Ba + 7aq.$ —Dark yellow needles, very soluble in water.

·7628 grm. lost ·1678 grm.  $OH_2$  at  $160^{\circ}$ , equivalent to 21·09 per cent.; calculated 20·72 per cent.

*Calcium Derivative*  $(C_6H_3NO_2ClO)_2Ca + 4aq.$ —Tufts of canary-yellow, silky needles, which become orange-yellow when anhydrous. Exposed to dry air it readily loses water.

·5676 grm. lost at  $150^{\circ}$  ·0835 grm.  $OH_2$ , equivalent to 14·7 per cent.; theory 15·75 per cent.

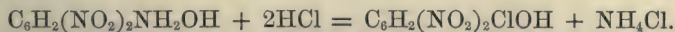
*Magnesium Derivative*  $(C_6H_3NO_2ClO)_2Mg + xaq.$ —Pale yellow, very soluble needles.

Pure orthonitrochlorophenol is readily converted by nitric acid of sp. gr. 1·36 into dinitrochlorophenol, melting at  $110^{\circ}$ — $111^{\circ}$ , and identical in all respects with the product of the chlorination of dinitrophenol.

I intend, so soon as I have obtained a sufficient quantity of this phenol, to reduce it to monochlorophenol, and to determine by fusion with potassium hydrate to which of the three dihydroxybenzols this latter corresponds.

Diazonitrophenol from dinitrophenol is readily decomposed by hydrochloric acid; the nitrochlorophenol so formed is, it would seem, different from either of the known nitrochlorophenols, but I have not yet obtained it pure in sufficient quantity to decide this point.

I may here mention, in reference to Faust's formation of dinitrochlorophenol by the action of hydrochloric acid on diazodinitrophenol, that a number of experiments in somewhat the same direction with picramic acid and hydrochloric acid were unsuccessful; it was hoped that reaction might take place according to the equation:—



Similarly the action of ammonia on dinitrochlorophenol, in the hope of obtaining amidodinitrophenol gave no result; at low temperatures no reaction was obtained, and at higher temperatures only resinous products were formed. I believe, however, that this reaction will be



realisable with bromo- or iodo-dinitrophenols, and am at present engaged with experiments in this direction.

*Dichlorophenolsulphonic Acid from Dichlorophenol.*

In my former communication I stated that, by chlorination of phenolmetasulphonic acid and subsequent nitration of the product, nitrodichlorophenol (melting at  $121^{\circ}\cdot 5$ ) was obtained, the same as is formed by direct nitration of dichlorophenol, prepared by the action of chlorine on phenol. It seemed probable, therefore, that by converting dichlorophenol into sulpho-acid, a dichlorophenolmetasulphonic acid might possibly be obtained, identical with that formed by chlorination of phenolmetasulphonic acid. In order to test this hypothesis, a quantity of dichlorophenol was acted upon by fuming sulphuric acid, and after removal of the excess of the latter, a potassium salt prepared, which (in the dry state) was at once treated with nitric acid, sp. gr.  $1\cdot 36$ , in excess, without cooling. A nitro-product was thus obtained which gave an orange-yellow potassium derivative, from which, by decomposition with dilute acid, pure dinitrochlorophenol melting at  $103^{\circ}$  was separated; this seems to have been the only product of the reaction, no dichloronitrophenol ( $121^{\circ}\cdot 5$ ) whatever being formed. This phenol is, I believe, from the composition of its sodium, calcium, and magnesium salts, identical with the dinitrochlorophenol which Dr. Stenhouse obtained by the action of chloride of iodine on picric acid. It bears in all respects a very remarkable resemblance to dinitrochlorophenol, melting at  $110^{\circ}$ — $111^{\circ}$ , and these two isomerides are no doubt very closely related: so far as I have at present ascertained, the corresponding metallic derivatives of each contain the same number of molecules of water of crystallisation; but whereas the salts, and solutions of the salts, of that melting at  $110^{\circ}$ — $111^{\circ}$  are yellow, those of the phenol melting at  $103^{\circ}$  are deep orange-yellow. I hope shortly to be able to give an account of the metallic derivatives of the  $103^{\circ}$  melting point phenol obtained both from picric acid and from dichlorophenol, as well as of the amidonitrochloro- and nitrochloro-phenol derived from it. The amidonitrochlorophenol crystallises in fine, deep bronze-yellow needles. Experiments are also in progress to determine the action of nitric acid *in the cold* on the above dichlorophenolsulphonic acid, which it is to be expected will yield under these conditions a nitrodichlorophenol.

I may mention that, in order to confirm the results obtained in the chloro-series, I have for some time past been engaged, in conjunction with my friend, Mr. Leonard, in comparing the bromonitrophenols obtained respectively—(1) by bromination of dinitrophenol; (2) by nitration of orthonitrobromophenol; (3) by nitration of dibromophenol

parasulphonic acid; (4) by the action of hydrobromic acid on diazo-dinitrophenol.

It would seem to be generally assumed that in picric acid the three nitro-groups occupy contiguous positions; but whereas the grounds on which two of these groups, those which are contained in dinitrophenol, have been placed in the positions 2 : 3 are evident, it is not easy to discover on what experimental data the third group is considered to occupy the para (4) position. That it is this third group which is reduced on treatment with ammoniac sulphide, is proved by the reduction of picramic acid by Griess's method to ordinary dinitrophenol. Faust, as I have above remarked, has lately shown that dinitrochlorophenol melting at  $111^{\circ}$  is obtained by the action of hydrochloric acid on diazodinitrophenol from picramic acid: consequently, if the third nitro-group in picric acid be in the para (4) position, then the chlorine in this dinitrochlorophenol, which is obtained by replacement of this nitro-group by chlorine, must also occupy the para (4) position. I have shown, however, that, on nitration of dichlorophenolparasulphonic acid, orthonitrodichlorophenol is formed, which, by the action of nitric acid, may be converted into dinitrochlorophenol identical with that obtained by Faust. Since in the phenolsulphonic acid from which the above dichloro-acid is derived, the  $\text{SO}_3\text{H}$  group occupies the para (4) position, a proof of which is that it yields resorcin on fusion with potassic hydrate, it is clear that neither of the chlorine-atoms in orthonitrodichlorophenol, or the one chlorine-atom in dinitrochlorophenol can also occupy that position, from which follows that in picric acid the nitro-groups are not all contiguous. In connection with this it will be interesting to ascertain whether the two trichlorophenols into which it will no doubt be possible to convert the two nitrodichlorophenols (melting at  $122^{\circ}$  and  $125^{\circ}$ ) are isomeric or identical amongst themselves and with the known trichlorophenol.

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### III.—*The Globe Siphon.*

By F. W. HART.

THIS instrument consists of a siphon having a globe or other-shaped reservoir connected with its apex, for the double purpose of starting the action and holding a supply of liquid to prevent the rupture of the column in the limbs of the siphon through disengagement of gas from the liquid, or accidental admission of air. The arrangement is found useful in drawing off liquids from precipitates, the filter being

attached to one limb of the siphon, or in washing precipitates holding gas or air loosely among their particles.

Professor McLeod observed that he had seen an instrument of very similar construction in use some five or six years ago in the laboratory of the Royal Institution.

Mr. Hart stated that it was now about five years since he had first made one of these siphons, and as far as he had been able to ascertain no account had yet been published.\*

Mr. A. Vernon Harcourt said that he had had a siphon in use for a considerable time precisely similar to the one described. It is employed to maintain a constant level in the still of a distilled water apparatus, by supplying it with warm water from the worm-tub of the condenser.

\* A figure of a siphon in every way similar to Mr. Hart's, except that it is furnished with a brass stopcock, is given in Griffin's *Chemical Handicraft*, 1866, p. 178, fig. 1709.

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# ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

## Physical Chemistry.

### Researches on Ammoniacal Salts with Weak Acids (*continued*).

By BERTHELOT (Compt. rend., lxxiii, 951—955, 1003—1007).

THE opinion generally entertained that no thermal effects are produced by mixing neutral salts is not justified by the behaviour of the salts with weak acids. Whilst the carbonates of potassium and sodium and the bicarbonate of ammonium are not only not decomposed by water, but do not evolve any heat when mixed with neutral salts of the alkalis, it is found that the neutral carbonates of the alkalis absorb heat on being brought together with the neutral ammonium carbonate, and liberate heat with the bicarbonate of ammonium. Neutral ammonium carbonate mixed with potassium or sodium carbonate liberates heat.

Ammonium bicarbonate is decomposed by the carbonates of potassium and sodium, heat being absorbed, whilst it evolves heat when mixed with neutral ammonium carbonate.

Ammonia alone does not produce any reaction with potassium carbonate.

These facts, illustrated by numerous data in the original paper, can only be explained on the supposition that neutral ammonium carbonate does not exist as such in its aqueous solution, but that part of it splits up into bicarbonate and free ammonia. If, then, potassium bicarbonate be present, it is neutralised by the ammonia. The action of the ammonium bicarbonate upon the neutral potassium salt is to be explained as a double decomposition, inasmuch as potassium bicarbonate is formed, together with neutral ammonium carbonate, which again splits up in the manner already described. Whatever the original state of things may have been, the final equilibrium arrived at is always the same, giving rise simultaneously to five compounds, viz., the neutral carbonate of potassium (or sodium) and ammonium, the bicarbonates of the same bases, and free ammonia.

As the bicarbonate of ammonium does not show any thermic reactions when brought into contact with the neutral salts or with the bicarbonates of potassium and sodium, and as the difference of the heats of combination of the bicarbonates of potassium and ammonium is the same as the difference of the heats of combination of the potassium and ammonium salts with strong acids, it appears that ammonium bicarbonate in presence of water is quite as stable as the bicarbonate of potassium and sodium.

From this the author concludes that it is not the gaseous tension of ammonia and carbonic acid exhibited in the solid ammonium carbonates which causes these salts in their aqueous solution to change their states of equilibrium.

The partial breaking up of ammonium bicarbonate in presence of water may be compared with the partial decomposition of the alcohols, the ethers, and sodium borate by water. As it seems that at the ordinary temperature the products of these decompositions are quite stable in presence of the compound which has furnished them, as for instance acetic hydrate and alcohol in presence of acetic ether, it is not advisable to characterise these complex systems of equilibrium, formed by an alcohol, an acid, an ether, and water, or by the bicarbonates of ammonium, ammonia, and water, as cases of dissociation, as it would deprive this term of its new and definite signification.

During the formation of one equivalent of neutral ammonium carbonate, quantities of heat are set free which vary—

1. With the concentration—

From 6.2 to 5.3 heat-units, when the quantity of water at (about) 20° c. varies from 110 H<sub>2</sub>O to 1100 H<sub>2</sub>O<sub>2</sub>.

2. With the temperature—

From 6.1 to 6.4 heat-units, when the temperature varies from 15° to 22°, in presence of 110 H<sub>2</sub>O.

Evolution of heat is increased by the presence of an excess of base, contrary to what takes place in the case of neutral salts with fixed alkali-bases:

CO <sub>2</sub> * + NH <sub>3</sub> , in presence of 110H <sub>2</sub> O <sub>2</sub> , evolve + 6.17 heat-units.	
CO <sub>2</sub> + 2NH <sub>3</sub> "           220H <sub>2</sub> O <sub>2</sub> "   + 6.81           "	
CO <sub>2</sub> + 3½NH <sub>3</sub> "           385H <sub>2</sub> O <sub>2</sub> "   + 7.03           "	

The heat of combination increases also with the degree of concentration:

CO <sub>2</sub> + NH <sub>3</sub> , in presence of 63½H <sub>2</sub> O <sub>2</sub> evolve + 6.40 heat-units.	
CO <sub>2</sub> + 1½NH <sub>3</sub> "           72 H <sub>2</sub> O <sub>2</sub> "   + 6.95           "	
CO <sub>2</sub> + 2 NH <sub>3</sub> "           80½H <sub>2</sub> O <sub>2</sub> "   + 7.19           "	
CO <sub>2</sub> + 2½NH <sub>3</sub> "           89 H <sub>2</sub> O <sub>2</sub> "   + 7.29           "	
CO <sub>2</sub> + 3 NH <sub>3</sub> "           97½H <sub>2</sub> O <sub>2</sub> "   + 7.35           "	
CO <sub>2</sub> + 3½NH <sub>3</sub> "           106 H <sub>2</sub> O <sub>2</sub> "   + 7.39           "	

The heat evolved increases with the quantity of ammonia present, and probably approaches the extreme limit 8.8, which would be the total heat of combination, if the quantities of heat evolved in the formation of the neutral carbonates of ammonium and potassium differed as much from each other as those liberated in the formation of the ammonium and potassium salts with strong acids.

The above results seem likewise to confirm the conclusion already referred to, that equivalent quantities of carbonic acid and ammonia when dissolved in water, combine only partially to form the two carbonates, whilst some of the ammonia remains free. If this be true, the following reactions can be explained.

"When equivalent quantities of neutral potassium carbonate and ammonium bicarbonate are brought together, the first products formed are monopotassium and diammonium carbonate, the latter of which, breaking up in the presence of water, causes heat to be absorbed. The

measurement of the quantity of heat actually evolved proves that the decomposition is incomplete in the presence of only one, but complete in the presence of two equivalents of the neutral potassium salts."

On mixing monopotassium and diammonium carbonate, heat is evolved.

Neutral potassium and ammonium carbonates mixed in presence of water give rise to an absorption of heat.

On the supposition that the heat of combination is really 8.8, we can, from the heat actually evolved in a particular case of neutralisation, determine numerically the state of equilibrium of the system formed. For instance,  $\text{CO}_2 + \text{NH}_3$  acting upon each other in presence—

of  $63\text{H}_2\text{O}_2$ , evolving 6.40 heat-units, give  $0.30\text{C}_2\text{O}_4\text{AmOH} + 0.40\text{CO}_3\text{Am} + 0.30\text{NH}_3$ .

of  $110\text{H}_2\text{O}_2$ , evolving 6.17 heat-units, give  $0.333\text{C}_2\text{O}_4\text{AmOH} + 0.333\text{CO}_3\text{Am} + 0.333\text{NH}_3$ .

of  $220\text{H}_2\text{O}_2$ , evolving 5.80 heat-units, give  $0.38\text{C}_2\text{O}_4\text{AmOH} + 0.24\text{CO}_3\text{Am} + 0.38\text{NH}_3$ .

of  $1100\text{H}_2\text{O}_2$ , evolving 5.30 heat-units, give  $0.44\text{C}_2\text{O}_4\text{AmOH} + 0.12\text{CO}_3\text{Am} + 0.44\text{NH}_3$ .

In general, it is proved that any system formed by a mixture of ammonia, carbonic acid, and water, always tends to the same state of equilibrium, whatever its original conditions may have been. When the original state of combination is less advanced than that required for the existence of equilibrium, heat will be evolved, the reaction becoming exothermic, whilst the reaction will be endothermic, when the original state of combination is more advanced than that corresponding to the state of equilibrium. These cases of incomplete combination do not allow the application of the general principle of exothermic reactions which holds good for the complete combinations.

It is this state of incomplete combination, that is to say, the manner in which the base of a salt divides itself between acid and water, which characterises the weak acids, and will in future enable us to define more precisely than before the vague terms *weak and strong acids and bases*.

The neutral salts formed by *strong acids* are stable, inasmuch as the addition of water or an excess of base does not give rise to any decomposition or other reaction, indicated by the thermometer. *Weak acids*, on the other hand, form with most of the strong bases, and especially with ammonia, salts capable of being decomposed by water. The author found this same contrast between the strong and weak acids in his researches on the double decomposition of salts.

R. S.

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**Thermo-Chemical Researches on the Ammonia Salts.** By M. BERTHELOT (Compt. rend., lxxiii, 1050—1059).

USUALLY a reciprocal action takes place between two salts in solution: the thermal phenomena observed indicate that the strong acids combine, by preference, with the strong bases, leaving the weak acids to



combine with the weak bases, so that the salt most stable in the presence of water, and as a necessary consequence the one least stable, are formed. A great number of experiments are given in illustration.

1st. *Both Salts formed with Strong Acids.*—When solutions of two neutral and stable salts are mixed, a feeble thermal effect is produced, which is not the sum of the effects produced by pure water on the two solutions separately, taken at the same temperature. Hence it follows that the saline thermoneutrality of Hess is never exact.

2nd. *One Salt formed with a Strong, and one with a Weak Acid.*—The action of the following alkali-salts on salts of ammonia has been examined: neutral carbonates, bicarbonates, phenates, borates, cyanides and sulphhydrates. The general results are that the potash or soda always combines with the stronger acid, leaving the ammonia to combine with the weaker. If the ammonium salt formed is stable in presence of water, the thermal effects produced by the mixing are but slight; if on the other hand the ammonium salt produced is decomposed by water, as the carbonate for example, an appreciable absorption of heat is the result.

3rd. *Both Salts formed with Weak Acids.*—Salts examined. Carbonates and cyanides, carbonates and phenates, carbonates and borates.

According to the author, all the facts brought forward in the paper show, that double decomposition takes place between salts in solution, by which the compound most stable under the conditions of the experiments is always formed chiefly, if not exclusively. A. D.

### **Thermo-Chemical Researches on Dissociation.** By P. A. FAVRE and C. A. VALSON (Compt. rend. lxxiii, 1144 to 1152).

WHEN any crystalline salt is dissolved in water, a variety of phenomena take place; for instance, in the case of a crystal of sodium sulphate ( $\text{NaSO}_4 + 10\text{HO}$ )\* it may be conceived, in the first place, that there is a disaggregation of the molecules which compose the crystalline edifice, and that, moreover, there is an effect corresponding to fusion. The latter is probably of a complex nature, being accompanied (1) by the dissociation of the chemical molecules, and (2) by the separation of the water associated with the salt to form the crystal, or by the addition of more water to it. In order to render this phenomenon sensible, it is necessary to resort to thermochemical methods; but, even then, serious difficulties present themselves: for, although the association of molecules will give heat, and their dissociation cold, still, the final result will represent only the difference between these two, and in the present state of science this difficulty cannot be resolved directly, although the results already obtained give hopes that it may be overcome.†

The sulphates have many advantages for this investigation, as they differ considerably in their crystalline form; and while some are

\*  $\text{O} = 8$ ;  $\text{S} = 16$ .

† This problem resembles that of simultaneous equations of several unknown quantities in algebra, requiring, in order to solve it, as many independent equations as there are unknown quantities.

anhydrous and others contain more or less water of crystallisation, many of them, being isomorphous, are capable of crystallising together. These salts have been examined in the crystalline state, either anhydrous or containing more or less water of crystallisation, and in the state of salts partially dehydrated by heat or by treatment with alcohol. Table I, contains the results obtained with salts of various degrees of hydration; Table II, those given by isomorphous salts crystallised together.

TABLE I.

Substance.	Heat units.	Substance.	Heat units.
$\text{FeSO}_4 \cdot 7\text{HO}$ .....	- 2182	$\text{MgSO}_4 \cdot \text{HO}$ .....	5493
$\text{ZnSO}_4 \cdot 7\text{HO}$ .....	- 2074	$\text{CuSO}_4 \cdot \text{HO}$ .....	4734
$\text{MgSO}_4 \cdot 7\text{HO}$ .....	- 1860	$\text{MnSO}_4 \cdot \text{HO}$ .....	4216
$\text{NiSO}_4 \cdot 7\text{HO}$ .....	- 1944	$\text{CdSO}_4 \cdot \text{HO}$ .....	3010
$\text{CoSO}_4 \cdot 7\text{HO}$ .....	- 1680	$\text{MgSO}_4$ .....	10152
$\text{CuSO}_4 \cdot 5\text{HO}$ .....	- 1216	$\text{ZnSO}_4$ .....	9289
$\text{MnSO}_4 \cdot 5\text{HO}$ .....	+ 235	$\text{CuSO}_4$ .....	8149
$\text{CdSO}_4 \cdot 3\text{HO}$ .....	+ 1531	$\text{MnSO}_4$ .....	7085
$\text{NaSO}_4 \cdot 10\text{HO}$ .....	- 9300	$\text{CdSO}_4$ .....	5344
$\text{ZnSO}_4 \cdot \text{HO}$ .....	+ 4812	$\text{NaSO}_4$ .....	354
$\text{ZnSO}_4 \cdot 3 \cdot 75\text{HO}$ .....	+ 2205	$\text{KSO}_4$ .....	- 3170
$\text{ZnSO}_4 \cdot 4 \cdot 46\text{HO}$ .....	+ 1354	$(\text{NH}_4)\text{SO}_4$ .....	- 975
$\text{ZnSO}_4 \cdot 4 \cdot 55\text{HO}$ .....	+ 1198		
$\text{ZnSO}_4 \cdot 6 \cdot 17\text{HO}$ .....	- 397		

TABLE II.

Substance.	Heat units.	The crystals contain
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Copper sulphate and zinc sulphate crystallised together.

$\text{ZnSO}_4 \cdot 5\text{HO}$ .....	- 1166	23·28 per cent. $\text{ZnSO}_4 \cdot 5\text{HO}$ .
$\text{CuSO}_4 \cdot 7\text{HO}$ .....	- 2060	44·30 per cent. $\text{CuSO}_4 \cdot 7\text{HO}$ .

Copper sulphate and magnesium sulphate crystallised together.

$\text{MgSO}_4 \cdot 5\text{HO}$ .....	- 1194	10·94 per cent. $\text{MgSO}_4 \cdot 5\text{HO}$ .
$\text{CuSO}_4 \cdot 7\text{HO}$ .....	- 2130	47·37 per cent. $\text{CuSO}_4 \cdot 7\text{HO}$ .

It will be observed that the anhydrous sulphates give very different numbers, although they are mostly positive, and that this difference disappears as the number of equivalents of water in the crystal increases. Hence it appears that the greater part of the heat evolved during the solution of an anhydrous salt, or of a salt in a state of hydration inferior to its normal state, is due to the formation of the crystal which contains the normal proportion of water. Moreover, the heat due to the combination of the first molecule of water, greatly exceeds that due to the succeeding molecules: thus between anhydrous magnesium sulphate and the same with one equivalent of water, there is a difference of 4659 heat-units for the addition of one equivalent

of water, whilst between magnesium sulphate with five and that with seven equivalents, there is only a difference of 666 for two equivalents of water.

Another question now arises as to what is the state of a salt partly dehydrated by alcohol? It will be found, by interpolation of the numbers in Table I, that the number of heat-units corresponding to zinc sulphate dehydrated by alcohol and containing five equivalents of water, is 1000, whilst zinc sulphate with five of water, obtained by crystallisation with copper sulphate, gives — 1166, being a difference of 2166 heat-units.

Again, with regard to double salts, it is found by experiment that the amount of heat set free by the solution of one of two salts remains sensibly the same, even if the water already contains the other salt in solution, so that if two salts are dissolved in water, the total amount of heat is the same as the sum of the two determined separately. If, however, they exist crystallised together as a double salt, they give a very different result:—

Substance.	Heat units.	A. Sum.	Substance.	B. Heat units.	Difference between A and B.
KSO <sub>4</sub> .....	— 3170	— 4386	{ Double salt, with 7HO.. }	— 7180	2794
CuSO <sub>4</sub> .5HO ....	— 1216				
(NH <sub>4</sub> )SO <sub>4</sub> .....	— 975	— 2191	{ Double salt, with 7HO.. }	— 5622	2431
CuSO <sub>4</sub> .5HO ....	— 1216				
KCl .....	— 4574	— 2251	{ Double salt, with 2HO.. }	— 3491	1241
CuCl.2HO .....	+ 2323				

It will be seen from the table that the amount of cold produced by double salts in dissolving is much greater than the sum of the amounts produced by the two salts dissolved separately. The author explains this by supposing that a certain amount of work is done in the formation of a double salt, giving rise to a disengagement of heat, and that when the double salt is dissolved, there is an inverse work of dissociation, characterized by cold; according to this supposition, the numbers in the column of differences represent the work of association or dissociation. Experiment also seems to establish a relation between the heat disengaged and the contraction which takes place when a salt is dissolved. If the density,  $d$ , of an anhydrous salt is known, the volume,  $V$ , occupied by an equivalent,  $p$ , can be deduced from it. When this equivalent is dissolved, say in a litre of water, it is easy to determine the increase of volume  $v$ . The difference  $V - v$  represents then the contraction of the salt on being dissolved, whilst  $\frac{V - v}{V}$  will represent the *coefficient of contraction* with respect to the original volume  $V$ .

The values of  $d$  in the following table are those given by Filhol; the values of  $v$  are deduced by methods to be published shortly by one of the authors.



Anhydrous salts.	$p$	$d$	$V = \frac{p}{d}$	$v$	$V - v$	$\frac{V - v}{V}$	$c$
KSO <sub>4</sub> .....	87 gr.	2·6	33	21	12	0·36	— 3170
NaSO <sub>4</sub> .....	71	2·6	27	10	17	0·63	354
CuSO <sub>4</sub> .....	80	3·5	22	4	18	0·81	8149
ZnSO <sub>4</sub> .....	80·75	3·4	23	4	19	0·83	9289
MgSO <sub>4</sub> .....	60·50	2·6	23	3	20	0·87	10152

In this table  $c$  is the number of heat-units, and it will be seen that they increase in the same ratio as the contraction  $V - v$ , or the coefficient of contraction  $\frac{V - v}{V}$ ; from this it would appear that the heat disengaged increases with the contraction effected in the substance, and is, at least partly, the immediate consequence of it.

C. E. G.

### Researches on the Thermal Effects produced during the Electrolysis of the Hydracids (*sequel*). By P. A. FAVRE (Compt. rend., lxxiii, 971).

THE author has examined the thermal effects observed during the electrolysis of hydrochloric, hydrobromic, and hydriodic acid. The diluted acids were placed in a voltameter furnished with a partition, so that the liberated haloïd was kept from contact with the hydrogen disengaged at the other pole. Under these circumstances, the heat absorbed in the voltameter will, after the necessary corrections, be the thermal equivalent of the analysis of the acid. The results are laid down in a series of tables. The author has also examined the thermal effects produced by substituting the above hydracids for sulphuric acid, in a Smee's battery. He comes to the conclusion that the numbers obtained as above, in the case of these hydracids, are really the thermal equivalents of their analysis; whereas, as previously pointed out by the author, the heat absorbed by oxyacids during their decomposition is the thermal equivalent of the analysis of water, and not of that of the acid. Finally, the author arrives at the conclusion that, in each voltaic couple, the molecules are electrolysed *successively*, and that when the *absolute number* of vibrations which correspond to a given intensity of the current has been determined, the *absolute weight* of the chemical molecules will be known.

A. D.

### On certain Phenomena observed in the Mutual Precipitation of Dilute Silver Solutions by the Chlorides, Bromides, and Iodides of Hydrogen and the Alkali-metals. By J. STAS (Compt. rend., lxxiii, 988—1002).

IN the precipitation of a silver solution by a chloride, a point is arrived at when a drop of a decimal silver solution produces a turbidity before the liquid has completely ceased to be rendered turbid by the addition

of chloride. With care, a point may be hit at which equal opalescence is produced by adding either a drop of decimal silver or of decimal chloride solution. When now, the liquid being divided into two parts, decimal chloride solution is added, drop by drop, to the one part, and decimal silver solution to the other, it is found that in the latter case the opalescence gradually increases, whilst in the first it diminishes.

When, on the other hand, the silver solution is precipitated by a decimal iodide or bromide solution until a further drop produces no more turbidity, it is found that after neutralising this last drop by a drop of decimal silver solution, the liquid remains perfectly clear on the addition of a decimal solution either of silver, or of alkaline bromide or iodide.

Gay-Lussac's method for the determination of silver in the wet way is founded on the supposition that silver chloride is absolutely insoluble in water and in acids; but in reality this compound is more or less soluble according as it exists: (*a*) in the gelatinous state; (*b*) in the curdy state; (*c*) in the state of powder; (*d*) in the granular, scaly, crystalline, or melted state. Of these modifications only *d* is completely insoluble in water of the ordinary temperature, whilst of the others, *b* is the most soluble.

The solution of *b* or *c* in pure or acidulated water can be completely precipitated by adding a solution of silver or of an alkaline chloride. The quantities of silver salt or of chloride, which are each capable of completely precipitating the silver chloride, are chemically equivalent to each other, and the silver and chlorine contained in them are three times as great respectively as the quantity of silver or of chlorine which is to be thrown down.

The solubility of the silver chloride is not at all influenced by the salts formed simultaneously with it, and is exclusively due to the pure acidulated water.

The presence of nitric acid increases the solubility of modification *c*, but not that of *b*.

A saturated solution of the granulated silver chloride is likewise precipitated by chloride or by silver-solution, and for every unit of silver thrown down, not less than three units of silver or of chlorine are required in the precipitating liquid. This modification cannot, however, be precipitated completely, as solutions containing less of it than  $\frac{4}{10}$  of the quantity required for saturation are not rendered turbid by decimal silver or chloride solution.

R. S.

### On Refraction and Dispersion in Selenium. By J. L. SIRKS (Pogg. Ann. cxliii, 429—439).

THE author has examined the refraction and dispersion in selenium by observing Newton's rings in thin layers of selenium, obtained by melting selenium between two plates of parallel glass.

The following table gives in column 2 the wave-lengths in thousands of a millimeter corresponding to the various Fraunhofer's lines in column 1; in column 3 the observed indices of refraction, and in columns 4 and 5, the same as calculated by means of Cauchy's and Christoffel's formulæ respectively.

A .....	0.7609	2.653	2.653	2.652
a.....	.7190	2.691	2.690	2.691
B .....	.6871	2.730	2.730	2.730
C .....	.6566	2.786	2.783	2.779
c.....	.6281	2.857	2.851	2.842
D .....	.5895	2.98	2.98	2.98

The dispersion in selenium is extremely great, as will be seen by the following table, giving the values of  $n_a - n_A$ ,  $n_B - n_a$ ,  $n_c - n_B$  and  $n_D - n_C$  for water, calcspar, bisulphide of carbon, and selenium; the numbers given are obtained from the real numbers by multiplying the latter so as to bring the value of  $n_C - n_A$  in each case to 100.

For water.....	36	31	33	88
For calcspar.....	36	30	34	90
For bisulphide of carbon ..	34	31	35	99
For selenium .....	29	30	42	146
				A. D.

### On the Spectra of Phosphorus and of Compounds of Silicon.

By G. SALET (Compt. rend. lxxiii, 1056).

WHEN the temperature of a hydrogen flame containing phosphorus, is lowered by directing against it a jet of water or air, the phosphorus spectrum observed consists of bands. Some of these bands correspond with lines seen in the line-spectrum of phosphorus; some appear to belong to a distinct order of spectrum.

The haloid compounds of silicon, when volatilised in the hydrogen flame, give spectra consisting of bands, rendered much more distinct by the use of the jet of air. The bands thus obtained agree generally in position with those of free silicon; they do not coincide with any of the more important lines in the electric spectrum of silicon. Fluoride of silicon, when volatilised in the flame, gives a continuous spectrum, but in Geissler's tubes it gives a magnificent spectrum of bands.

A. D.

### Observations on the Colour of Fluorescent Solutions: By

HENRY MORTON (Am. J. of Sci. [3] ii, 355).

AN abstract of a previous communication on the above subject was given in the last volume of this Journal, page 992. Since the publication of that paper, the author has noticed a certain phenomenon, which, while it in no respect affects the observations already recorded, or the general conclusions therefrom deduced, nevertheless renders negative some of the corroborative evidence which was previously offered in support of those conclusions.

It has been found that a very faint blue fluorescence is always visible in connection with the Geissler tubes in which the solutions were examined, and upon further experiment it was proved that any liquid whatever, when examined in this manner, was capable of exhibit-



ing the phenomena of fluorescence, although in itself it might be entirely destitute of fluorescent properties.

The explanation of this fact is simple. The greater portion of the feeble fluorescent light in passing from the glass to air will suffer total reflection at the outer surface of the glass; but if water or any other liquid be substituted for the air, the higher refracting power of the liquid will diminish the above reflection, and a larger quantity of light will reach the eye. The fluorescence of the tube being in this way increased, it naturally led to the supposition that the action was due to the liquid under examination. This fact renders valueless the experiments made with the vacuum-tube upon solutions of turmeric, but fresh observations with the spectroscope, in which extraneous fluorescence was eliminated, confirm the author's former conclusions as to the true colour of fluorescence in this liquid. The faint fluorescence noticed when solution of uranium nitrate was examined, can now be referred entirely to the above-mentioned phenomenon.

The author qualifies his former deduction, by stating that he does not assert that *all* solutions give a blue fluorescence, but simply those substances which he has examined.

J. W.

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**The Action of Light upon Chlorine and Bromine.** By E. BUDDÉ (Phil. Mag. [4], xlii, 290—294).

In the experimental prosecution of deductions drawn from the hypothesis that "the molecules of most elementary gases consist of two atoms," the author has arrived at some remarkable results with regard to chlorine and bromine.

Assuming the above theorem to be correct, it is natural to conclude that the so-called combination of two elementary gases must in general be preceded by the splitting up of their molecules into isolated atoms, and that consequently such a combination will be promoted by any influence which induces a separation of similar atoms, provided it does not at the same time hinder the combination of dissimilar atoms.

It is known that by insolation the chemical activity of chlorine is increased. The hypothesis advanced by the author in explanation of this fact assumes that light *tends* to resolve, or actually *does* resolve, the chlorine molecule into its constituent atoms—in other words, that light diminishes the force uniting Cl with Cl, and that occasionally, through the co-operation of light and internal motion (heat), a molecule,  $\text{Cl}_2$ , is actually split up into its constituents  $\text{Cl} + \text{Cl}$ . If the chlorine be pure, then the isolated atoms of chlorine will revolve like independent molecules between the undecomposed molecules  $\text{Cl}_2$ ; occasionally two of them will meet and reunite, so that finally, in case of a constant intensity of light, and constant temperature, there will be reached a state of dynamical equilibrium in which at any given moment, the number of molecules split up will exactly equal the number of molecules reproduced.

In a mixture of chlorine with hydrogen the separation of the molecular bonds of union would be facilitated by the affinity of the atom Cl for the foreign atom H, and combination would ensue as soon as

molecular disruption had taken place; but in free chlorine there would always of necessity exist a certain proportion of uncombined atoms, and from this fact, together with Avogadro's theorem, is drawn the conclusion that this gas, through insolation, *increases in specific volume*, the increase depending doubtless upon the intensity of the light.

Moreover, it is extremely probable that the reunion of chlorine atoms involves a production of heat; if so, the rays of high refrangibility would do a kind of work which would ultimately lead to a small stationary increase of temperature. The final conclusion drawn from this assumption is that chlorine, when exposed to *chemical rays*, will expand, but will contract to its original normal volume when no longer under the influence of light.

These propositions were tested by experiment in the following manner. A Leslie's differential thermometer was filled with chlorine, and oil of vitriol previously saturated with chlorine substituted for the index fluid. The bulbs were then placed so that either of them could be illuminated by any portion of the solar spectrum, while the variation in the position of the index during the action of the light was read off with the aid of a telescope.

As had been anticipated, a small expansion of the gas took place. When the bulb was exposed to the red and yellow portions of the spectrum, the displacement of the index amounted to about 1 millimetre, but a maximum of 6 to 7 millimetres was obtained when the bulb was illuminated by the violet and ultra-violet rays.

Control experiments were then made by exposing an ordinary differential thermometer to the action of the more refrangible rays, but no increase of temperature could be observed.

A differential thermometer, charged with carbonic anhydride and ether, behaved in the blue rays as in the previous instance. The contents of these bulbs should absorb heat to a much greater extent than when charged with chlorine.

A thermometer filled with chlorine was kept in a water-bath and exposed to direct sunlight. By alternately shading the one and the other of the bulbs, a displacement of the index amounting to several centimetres was obtained. This expansion is attributed essentially to the action of the chemical rays, more especially so, since it was found that when a thermometer filled with carbonic anhydride was placed under precisely similar circumstances, no action whatever was obtained.

The author is of opinion that the hypothesis which he has advanced, viz., that light actually decomposes chlorine molecules into chlorine atoms is no little supported by the fact that the rays which cause the expansion of chlorine coincide with those which are known to render it chemically active.

J. W.

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**On the Chemical and Mechanical Alterations of the Haloid Salts of Silver by Light.** By CARL SCHULTZ-SELLACK (Pogg. Ann. cxliii, 439—449).

THE author has examined the effect of light on the chloride, bromide, and iodide of silver. He shows that the effect is twofold—one a



chemical one, resulting in the liberation of the haloïd and the production of a subsalt insoluble in hyposulphite, the silver and the haloïd being separated by the light: the other is a mechanical effect, produced chiefly in presence of an excess of the haloïd, whereby the chemical action is entirely prevented, and consists in a disintegration of the particles of the haloïd salt, the particles becoming finer and finer as the action of the light continues. The latter phenomena may be imitated without the help of light. The results of the experiments is finally summed up as follows:—

1. Chloride, bromide, and iodide of silver suffer dissociation when exposed to the action of light; the vapour-tension due to this dissociation is small in the case of chlorine and bromine, extremely small in the case of iodine.

2. If the chemical decomposition of the silver salts is prevented by the presence of the free haloïds, they undergo a *mechanical disintegration*; in presence of substances absorbing the haloïds this effect is slight; by enclosing the silver salt in some solid substance, as varnish for example, this disintegration is prevented. Only the ultra violet, and the violet, perhaps down to the line G, have any action.

3. As the particles of the iodide of silver film become smaller and smaller, a series of colours are observed by transmitted light, due most probably to interference.

4. Even without the action of light, an iodide of silver film on collodium may be made to show the same series of colours, when it is produced in various degrees of subdivision, by rapid precipitation, or by slow solution of the precipitated film.

5. The behaviour of silver iodide, in presence of excess of iodine, may be utilised for the production of photographic pictures which may be termed *mechanical silver iodide pictures*. They are soluble in sodic hyposulphite.

6. *Chemical silver iodide pictures* obtained on a film of silver iodide which is either moistened with a silver solution, or rests on a surface of silver, consists, in the parts affected by the light, of subiodide of silver, which is *insoluble* in sodic hyposulphite. The *chemical* picture may be developed even after the removal of the soluble iodide of silver; the *mechanical* picture cannot be developed at all.

7. The process of photographic development is connected essentially with chemical decomposition. The surface film of subiodide, bromide, or chloride of silver, of extreme tenuity, possesses the remarkable property of fixing particles of nascent silver or mercury.

8. The haloïd salts of copper, on a copper support, can also be photographically developed by means of mercury.

A. D.

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**On the Colour of Opaque Media and on the so-called Colour Photography.** By C. SCHULTZ-SELLACK (Pogg. Ann. cxliii, 449—451).

IN a preceding paper the author showed that iodide of silver is converted into a powder when exposed to the action of light, the powder becoming finer the longer the exposure lasts. The colours shown



during this progressive comminution, brown, red, green, blue, greyish-white, must be looked upon as colours of a thin layer of the opaque medium when the size of the particles, and the intervals which separate them, are less than  $\frac{1}{4}$  wave length. That the colours are not interference colours of the individual particles (corresponding to the colours shown by thin plates) is shown by the fact that they are altered if the air contained in the interstices is replaced by water or varnish.

The colours obtained in so-called colour-photography are due, most likely, to a similar cause. The colour produced will depend on the time of exposure and the intensity of the light; the apparent specific action of various colours may be due entirely to the amount and intensity of violet light they contain. The production of colours corresponding to the colour of the light employed is thus entirely accidental, and the real problem remains unsolved.

A. D.

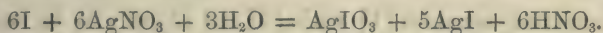
### Researches on the Invisible Photographic Image. By

H. VOGEL (Deut. chem. Ges. Ber., iv, 825—827).

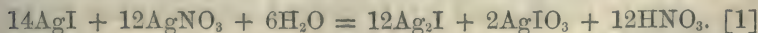
It has been already pointed out by the author that the substances which have been found capable of replacing argentic nitrate in rendering argentic iodide more sensitive to light, have the property of fixing free iodine, and that any other substance which possesses this property without of itself affecting argentic iodide, may also be employed instead of argentic nitrate. Further researches have confirmed these observations, but at the same time have disclosed an important difference in the behaviour of the argentic iodide to light, according as it is moistened with solution of argentic nitrate, or with one of the other sensitisers.

Argentic iodide, as was pointed out by the author seven years ago, exposed to light with solution of argentic nitrate, completely loses the imprint of the light by treatment with solution of potassium iodide, after which it becomes impossible to develop an image on it. He has since found, on the other hand, that, exposed to light with solution of potassium ferrocyanide, argentic iodide does not lose the imprint of the light by after-treatment with potassium iodide.

The cause of this difference must be attributed to the special reaction of iodine with solution of argentic nitrate.  $2\text{AgI}$  decompose into  $\text{Ag}_2\text{I}$  and  $\text{I}$ , and the latter forms with the silver solution, argentic iodide, argentic iodate, and free nitric acid:—



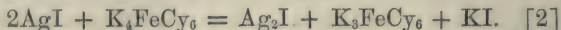
This reaction, taking place in presence of light, the  $\text{AgI}$  thus produced is at once further reduced by the excess of  $\text{AgNO}_3$  present, and forms argentous iodide. This reaction takes place thus—



The seat of the invisible image contains, therefore, argentous iodide, argentic iodate, and free nitric acid.

The decomposition is entirely different in presence of potassium

ferrocyanide. This salt, by taking up iodine from the argentic iodide, passes into potassium ferrieyanide and potassium iodide :



Now it is known how readily iodates in contact with iodides yield free iodine in presence of an acid. The same reaction also takes place when potassium iodide acts upon the photographic image formed upon argentic iodide in presence of argentic nitrate, [1] and the free iodine thus formed at once converts the argentous iodide into argentic iodide again, so that the image is destroyed.

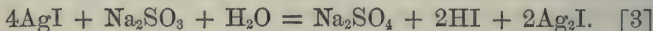
Such an effect is evidently impossible in the case of the image produced under potassium ferrocyanide, [2] since under the circumstances potassium ferrieyanide and potassium iodide do not decompose each other.

The loss of the invisible image observed by Lea to result from leaving it for a long time in the dark, and considered by him to be due to a physical change, admits of ready explanation on chemical grounds, as being the effect of an inversion of equation [1], the left side becoming the right.

These phenomena are, however, seriously interfered with if the silver-solution is impure, as is so frequently the case in practice, on account of the impurities derived by the bath from the collodion. The imprint of the light upon argentic iodide under solution of argentic nitrate, in presence of such organic substances, is not destroyed by after-treatment with potassium iodide. Very minute quantities of these matters are sufficient to cause this abnormal action of the silver-bath. The author has found .006 grms. of permanganate sufficient to destroy them in 1200 c.c. of abnormal 10 per cent. silver-bath, and to restore the bath to a normal condition.

It is remarkable, and as yet without explanation, that potassium ferrocyanide also destroys the imprint of the light upon argentic iodide under argentic nitrate, notwithstanding that this salt actually promotes very decidedly the change of the argentic iodide by light.

The decomposition which occurs in the presence of other iodine-fixing substances during the exposure of the argentic iodide to light, is analogous to that given in [2]. Usually there are formed an oxidation product and a body of the type of hydriodic acid, as, for example, with sodium sulphite :—



On comparing equation [1] with [2] and [3] it will be seen that 14 equivalents of argentic iodide exposed to light with the silver-solution yield 12 equivalents of argentous iodide, and only 7 with ferrocyanide and other bodies. This explains how it is that argentic nitrate gives images so much more intense than those formed with other sensitizers, and why the silver salt is to be preferred before all others for use in photography.

E. D.

## Inorganic Chemistry.

**On the Composition of Atmospheric Air and Rain-Water.** By R. ANGUS SMITH (Sixth and Seventh Reports of the Inspector under the Alkali Act of 1863).

IMPURITIES of the atmosphere may be discovered by an examination of the rain-water of the locality; or the air may be subjected to artificial washing, and these washings examined. The author has employed both methods. He considers the latter method as affording a more accurate comparison between different atmospheres, since the composition of rain-water necessarily varies according to the amount which falls in a given time, the rain of a dry season being far more impure than the rain of a wet season.

The author's examinations of rain-water are very numerous. The modes of determining the various impurities were in no case gravimetric, owing to the small volume of water at disposal. The ammonia, albuminoid ammonia, and nitric acid were estimated by Wanklyn, Chapman, and Smith's methods. The hydrochloric and sulphuric acids were determined from the quantity of water required to produce a certain standard amount of whiteness with solution of silver or barium. The permanganate test was applied to the acidified water, the experiment lasting a few minutes only. The more characteristic results are given in the accompanying table:—

RAIN WATER.—Average impurities per million parts.

Where collected.	Hydrochloric acid.	Sulphuric acid.	Sulphuric acid for 100 hydrochloric.	Free acids calculated as sulphuric acid.	Ammonia.	Albuminoid ammonia.	Nitric acid.*	Oxygen required as permanganate.
Ireland, Valencia.....	48·67	2·73	6	None	·18	·03	·37	·05
Scotland, five sea coast country places, west.....	12·28	3·61	29	·14	·48	·11	·37	·02
Scotland, eight sea coast country places, east.....	12·91	7·66	59	2·44	·99	·11	·47	·65
Scotland, twelve inland country places.....	3·38	2·06	61	·31	·53	·04	·31	·26
England, twelve inland country places.....	3·99	5·52	138	None	1·07	·11	·75	·47
Scotland, six towns (Glasgow excluded).....	5·86	16·50	282	3·16	3·82	·21	1·16	1·86
Darmstadt.....	·97	29·17	2998	1·74	—	—	—	—
London†.....	1·25	20·49	1645	3·10	3·45	·21	·84	—
England, six manufacturing towns.....	8·70	34·27	394	8·40	4·99	·21	·85	2·74
Manchester.....	5·83	44·82	768	10·17	5·96	·25	1·01	3·22
Glasgow.....	8·97	70·19	782	15·13	9·10	·30	2·44	10·04

\* Nitrous acid is here included.

† Average of a few specimens only.



It appears that the amount of chlorides in rain-water is dependent on the distance from the sea, and on the direction and force of the prevalent winds; the combustion of coal has a slight effect in increasing the quantity. Sulphuric acid is derived chiefly from the combustion of coal, but is also a product of vegetable and animal decomposition; it always increases as we proceed inland. In sea water the proportion of hydrochloric to sulphuric acid is 100 to 11·6; excess of sulphuric acid over this proportion is due to terrestrial contamination. Free acids are rarely found, save in the rain-waters of towns. Ammonia is chiefly connected with the combustion of coal, and to a lesser degree with the decomposition of organic matter. Albuminoid ammonia is related solely to animal and vegetable life. Nitric acid may be taken as a measure of "purified sewage." The permanganate test denotes a variety of products, both from coal and organic decomposition.

To examine air by washing, the author shakes 50 c. c. of water in an empty 2-litre bottle; then draws out the washed air by one stroke of a flexible bellows-pump  $1\frac{1}{2}$  times the capacity of the bottle; agitates as before the fresh air which has entered; and repeats the operations 10 to 100 times, according to the purity of the atmosphere. In this plan the volume of air used is only known approximately, the results are therefore comparative instead of absolute. The following are some of the results obtained by washing, the purest air being taken as 100:—

Locality of atmosphere.	Hydrochloric acid.	Sulphuric acid.	Locality of atmosphere.	Ammonia.	Albuminoid ammonia.
Blackpool .....	100	100	Inellan .....	100	100
Didsbury .....	277	320	London .....	117	116
Buxton .....	247	345	Metropolitan Railway ..	138	271
London .....	320	361	Glasgow .....	159	221
St. Helens .....	516	468	A bedroom .....	194	173
Manchester .....	369	549	Office at Manchester ..	235	194
Metropolitan Railway ....	974	1554	A midden .....	644	302

By means of these air washings a chemical climatology may be established.

The author has determined the amount of oxygen and carbonic acid occurring in air under a variety of circumstances; the more characteristic results are as under.

Where collected.	Oxygen per cent.	Carbonic acid per cent.
Tops of hills, Scotland .....	20·980	·0332
London, parks and open places .....	20·950	·0394
London (average of 68 analyses) .....	20·885	·0439
Glasgow, open places .....	20·929	·0461
Glasgow, closer places .....	20·889	·0539
Metropolitan Railway tunnels .....	20·700	·1452
Theatres, worst parts .....	—	·3200
Mines (average of 339 analyses) .....	—	·7850
When candles go out .....	18·500	—

**Researches on Ozone, Hydrogen Peroxide, and Ammonium Nitrite.** By H. STRUVE (*Zeitschrift für Anal. Chemie*, x, 292—298).

THE author refers to his former publications respecting the presence of hydrogen peroxide in the atmosphere; he then states that later researches, made in Asia, have confirmed his former results, and showed also the presence of ammonium nitrite. He concludes that ozone, hydrogen peroxide, and ammonium nitrite, are clearly connected; also that these are produced by all processes of combustion in the atmosphere, whether on the large scale, as in lightning flashes, or on the small scale, as in the combustion of hydrogen, carbon, &c., on the earth. He also refers to the labours of Schönbein, who, in 1861, showed that in the slow oxidation of phosphorus there are produced—in addition to ozone—phosphorous, phosphoric, nitrous, and nitric acids, ammonia, and hydrogen peroxide. Böttger also demonstrated the presence of hydrogen peroxide in the products of combustion of hydrogen and carbon. Loew, in 1869, showed the presence of ozone in flame.\*

The author now attempts to show that all three substances occur together in many phenomena of combustion. If a hydrogen flame be burned beneath a long, drawn-out funnel, the presence of ozone is easily shown at the upper opening of the funnel; and if the water on the sides of the funnel be collected and examined, hydrogen peroxide and ammonium nitrite are recognised by their behaviour with potassium iodide.

The author states that not only is ozone a product of the vital processes of all animals, but that ammonium nitrite also is present in the expired breath, in especially large quantities after eating.

The presence of hydrogen peroxide in expired breath is regarded by the author as not quite satisfactorily proved.

T. E. T.

**Decomposition of Nitric Acid by Heat.** By L. CARIUS (*Deut. Chem. Ges. Ber.*, iv, 828—834).

It is known that nitric acid is decomposed by heat, with formation of oxygen, water, and nitrogen peroxide. Its decomposition begins at the boiling point of the strongest acid (Mitscherlich), and must be complete at a red heat. The author believes he has determined, with apparently sufficient accuracy for all purposes, the nature of the products of this decomposition, its gradual increase with the temperature, and the point at which it becomes complete. This he has done by taking the vapour-densities of the products of the decomposition at different temperatures.

On account of the weakening of the acid during distillation, and the dependence of the degree of this upon the pressure (Roscoe), it became necessary to ensure, at the temperature of the decomposition, both the

\* See also Than, this Journal [2], ix, 483.

vaporisation of all the acid employed, and the thorough mixture of the resulting gases.

Two methods were adopted, in order to control the results. One was a modification of Dumas' method, consisting essentially in first effecting at the desired temperature the complete volatilisation of the acid, and the uniform mixture of the products in the *sealed* vessel, then reducing the tension to that of the air by a brief opening of the vessel and sealing it up again, and proceeding with the operation much as usual, the residual air and the oxygen from the nitric acid being measured, and correction made for the latter.

The other was a new method of taking vapour-densities, specially adapted for those cases where it is desired to employ easy and accurate weighing, and where it is not possible to work over mercury, as in Gay-Lussac's method. The substance is weighed in a sealed bulb, and placed in a wide glass tube, serving for the determination. This tube is then filled with an indifferent gas (in this case, air), drawn out to a long capillary point, and then sealed at known pressure and temperature. After breaking the bulb, the tube is heated and maintained for a sufficient length of time at a constant temperature (most conveniently in a vapour-bath formed of a larger tube enclosing it) and frequently rotated, so as to ensure thorough mixing of the gases. The drawn out extremity of the tube is then made to project from the bath, heated in the flame till it blows out, and, so soon as the tension has sunk to that of the air, re-sealed, the temperature of the bath, and the height of the barometer being at the same time read off. After cooling, the point of the tube is broken off under water, or a very dilute solution of soda, the quantity of the residual gas ascertained, and the capacity of the tube determined.

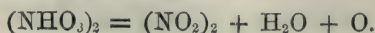
For calculating the volume,  $W'$ , of the vapour, and its specific gravity,  $s$ , we have—

$$W' = \frac{(V' - v')S^\circ}{v'} \text{ and } s = \frac{A}{W'} \times 773.$$

where  $A$  is the weight of the substance employed,  $S^\circ$  the volume of the indifferent gas (cubic contents of tube minus volume of liquid used),  $v'$  the volume of the latter after opening the tube in the flame (corrected for the oxygen set free, in the case of nitric acid), and  $V'$  the total volume of gas at the moment of sealing up again, all measurements being taken at  $0^\circ$  and 760 mm. Some test-experiments with bromine-vapour gave good results by this method.

A correction for the 0.45 per cent. of water which still remains in the strongest acid that can be obtained is unnecessary, as it falls within the limits of error of experiment.

The vapours formed from nitric acid at different temperatures show a decrease in specific gravity with an increase, but not proportionately to it, of the temperature up to about  $256^\circ$ , from which up to  $312^\circ$  the specific gravity has been found to remain constant. The specific gravity is then ( $H = 1$ ) almost exactly 18, that is,  $\frac{4}{7}$  of the specific gravity of nitric acid, vapour,  $\frac{6.3}{2}$ , or the number required by complete decomposition, according to the equation—





The author shows the improbability that either nitrous acid or nitric oxide is formed by the decomposition of nitric acid, and concludes therefore that the only one that occurs is that according to the above equation, and that this is complete at about  $256^{\circ}$ .

He gives a formula for calculating the extent per cent. of the decomposition by which the following table has been calculated. In it the specific gravities of the mixed vapours from nitric acid, at temperatures up to  $256^{\circ}$ , have been obtained from the direct results by interpolation. The two given above  $256^{\circ}$  are direct results.

Temperature of Decomposition.	Sp. gr. H = 1.	Decomposition per cent.	Oxygen from 1 grm. $\text{NHO}_3$ .
86°	29·6	9·53	8·43 c.c.
100	29·1	11·77	10·41 „
130	27·6	18·78	16·62 „
160	25·8	28·96	26·22 „
190	23·0	49·34	43·69 „
220	20·4	72·07	63·77 „
250	18·6	93·03	82·30 „
256	18·0	100·00	88·47 „
265	17·9	—	—
312	17·8	—	—

E. D.

**On the Hydrochlorides of Hydroxylamine.** By W. LOSSEN  
(Zeitsch. f. Chem. [2] vii, 326—329).

ON mixing a concentrated aqueous solution of 1 mol. hydroxylamine hydrochloride,  $\text{NH}_3\text{O}.\text{HCl}$ , with a solution of 1 mol. hydroxylamine in absolute alcohol, the salt  $2\text{NH}_3\text{O}.\text{HCl}$  separates in large thin crystals or in needles. By dissolving it at a very gentle heat in a small quantity of water, and cooling, or evaporating the solution over sulphuric acid, it is obtained in apparently rhombic prisms, whilst in the mother-liquors the sesquihydrochloride,  $3\text{NH}_3\text{O}.\text{HCl}$ , is contained; this salt is best obtained by dissolving  $\text{NH}_3\text{O}.\text{HCl}$  and  $2\text{NH}_3\text{O}.\text{HCl}$  in a little water at a gentle heat. It forms large crystals, showing a great number of faces, and belonging probably to the rhombic system. On addition of absolute alcohol to the mother-liquor of these crystals, the semihydrochloride crystallises out, a fact which seems to be in contradiction to the observation that the mother-liquors of the semihydrochloride give, on addition of alcohol, crystals of the sesquihydrochloride; but these solutions contain not only the sesquihydrochloride, but also the normal salt, as on evaporation of the solutions of  $2\text{NH}_3\text{O}.\text{ClH}$ , or  $3\text{NH}_3\text{O}.\text{HCl}$ , in the water-bath, they are converted into  $\text{NH}_3\text{O}.\text{ClH}$ .

The semihydrochloride and the sesquihydrochloride are deliquescent in damp air, very sparingly soluble in alcohol and insoluble in ether. The former salt melts at  $85^{\circ}$ , and the latter at  $95^{\circ}$ ; at the same time a slight evolution of gas taking place, which becomes violent on applying stronger heat. Both salts precipitate ferric chloride solution and reduce mercuric chloride, chromic acid, and silver nitrate. The sesquihydrochloride produces a green precipitate in a solution of

copper sulphate, which disappears on shaking, a dark blue solution being formed, which soon becomes colourless, cuprous chloride separating out. The semichloride produces a similar reaction, but the green precipitate redissolves but slowly or not at all, being also converted after some time into cuprous chloride. On heating either of the salts with platinic chloride solution, gases are evolved, and a colourless solution is obtained, from which after concentration the compound  $4\text{NH}_3\cdot\text{OPtCl}_2$  crystallises in colourless needles, is insoluble in alcohol, and undergoing violent decomposition on heating. On adding silver nitrate to its solution, only a part of the chlorine is precipitated.

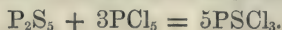
C. S.

**Contributions to the History of the Phosphorus Chlorides.** By  
T. E. THORPE (Phil. Mag. S. 4, vol. 42, 305).

1. *Reduction of Phosphoryl Trichloride.*—The author has attempted to supply one of the missing links in the chain of analogies pointed out by Roscoe as existing between vanadium and phosphorus. He sought to obtain phosphoryl dichloride in a manner analogous to that by which Roscoe obtained vanadyl dichloride, namely, by heating the trichloride with zinc in a sealed tube to a high temperature. A quantity of the pure liquid was sealed up together with zinc filings in a tube and heated to about  $400^\circ$ . The zinc was slowly acted upon, and a transparent glassy mass was formed at the bottom of the tube. The small quantity of liquid remaining was submitted to distillation; it began to boil at about  $80^\circ$ , the thermometer gradually rising to  $105^\circ$ , by which time the whole of the liquid had passed over. This behaviour appeared to indicate the presence of phosphorus trichloride,  $\text{PCl}_3$ ; and a few drops of the liquid decomposed by water yielded the reactions of phosphorous acid. The quantity was too small to admit of fractional distillation. It was analysed with the following results:—Cl 73.21 per cent.; total P. 21.09 per cent.; P. giving  $\text{PO}_4\text{H}_3$  on treatment with  $\text{H}_2\text{O}$ , 10.58 per cent.

These numbers correspond almost exactly to a mixture containing equivalent quantities of  $\text{POCl}_3$  and  $\text{PCl}_3$ . The action of zinc at a high temperature on phosphoryl trichloride is therefore different from the action of this metal on the corresponding vanadium compound. In the former case the reaction is attended with abstraction of oxygen; in the latter with abstraction of chlorine.

2. *Preparation of Phosphorus Sulphochloride.*—This compound, first obtained by Serullas by the action of sulphuretted hydrogen on pentachloride of phosphorus, and afterwards prepared by Baudrimont by the action of pentachloride of phosphorus on antimony trisulphide, can, according to the author, be more easily obtained by the action of phosphorus pentachloride upon phosphorus pentasulphide:



The materials mixed in the proportion indicated by this equation are heated together; in a few minutes the mass liquefies to the phosphorus sulphochloride, which, after a single distillation, is obtained perfectly pure.

T. E. T.

**Preliminary Communication on the Action of Phosphorus Oxychloride on Phosphoric Anhydride.** By G. GUSTAVSON (Deut. Chem. Gez. Ber. iv, 853).

By heating equal quantities of phosphorus oxychloride and phosphoric anhydride in sealed tubes for 36 hours, the author obtained a semi-fluid transparent mass, which he supposes to be meta-phosphoric chloride ( $\text{PO}_2\text{Cl}$ ), or a mixture of this with a polymeride. He represents the reaction thus:— $\text{P}_2\text{O}_5 + \text{POCl}_3 = 3\text{PO}_2\text{Cl}$ .

C. C.

**On the Behaviour of Sulphurous Acid towards Phosphates and similar Compounds.** By B. WILHELM GERLAND (J. pr. Chem. [2] iv, 97—139).

THE author describes the differences of the action of sulphurous acid in a watery solution upon different phosphates. Some are simply dissolved, while others are completely decomposed, a sulphite being formed, and phosphoric acid going into solution. From some compounds sulphurous acid withdraws a part of the base, so that from a basic compound a neutral or acid compound is produced; upon others, viz., tricalcium phosphate, sulphurous acid acts in a way, different from any of the foregoing.

The results, which are very fully described in a lengthy paper, may be summed up as follows:—

1. Tricalcium phosphate is easily soluble in sulphurous acid. Concentrated solutions are decomposed at temperatures above  $18^\circ$ , forming mono- and dicalcium phosphate and calcium sulphite. Both concentrated and dilute solutions are decomposed into dicalcium-hydrogen phosphate and calcium sulphite by alcohol, when placed at ordinary temperatures, in a vacuum, or more quickly by boiling under diminished atmospheric pressure. But by quickly heating and boiling at the ordinary pressure, crystals are deposited from the solutions, of a new substance, called by the author *tricalcium phosphato-sulphite*.

This substance, to which, as the result of a number of analyses, the author gives the formula  $\text{Ca}_3\text{P}_2\text{O}_8\text{SO}_2 + 2\text{H}_2\text{O}$ , forms a white crystalline precipitate when sulphurous acid is passed into a watery solution, in which tricalcium phosphate is suspended. After complete solution of the phosphite is effected, the liquid is quickly boiled, and the precipitate collected.

This substance differs from the above-mentioned mixture of dicalcium phosphate and calcium sulphite by its great stability; it may be heated to  $110^\circ$  without decomposition, but at a somewhat higher temperature it is broken up, watery vapour, mixed with sulphurous and sulphuric acid vapour and sulphur, being given off.

This tricalcium phosphato-sulphite possesses disinfectant properties in a marked degree; it is stable, has no smell, is tasteless, does not affect linen or woollen cloths, and is obtained in a very handy form, as a heavy, white, dry powder.



A small quantity mixed with decaying animal matter at once removes its bad odour.

Although unchanged in pure air, it undergoes slow oxidation when placed in air containing decomposing animal matter.

The corresponding compounds of the other metals have not been obtained.

2. Dicalcium-hydrogen phosphate is easily soluble in sulphurous acid, the phosphate being again obtainable from this solution, unchanged. All these solutions retain the gas which they have absorbed with great energy, but the basic do so more energetically than the neutral phosphates.

3. Basic and neutral magnesium phosphate and magnesium-ammonium phosphate are easily dissolved by water containing sulphurous acid, the first two without decomposition; the last when in excess, gives neutral magnesium phosphate.

4. Basic and neutral manganese phosphate behave in a similar manner to the magnesium phosphates. In the cold the solutions yield crystals composed chiefly of the neutral phosphate; by boiling, the crystalline basic phosphate is precipitated.

5. Copper phosphate is only slightly dissolved by sulphurous acid solutions. At ordinary temperatures crystals of cuproso-cupric sulphite are deposited; by boiling, a copper phosphate, probably of the same composition as the original phosphate, is obtained.

6. Uranium phosphate is but slightly soluble in sulphurous acid, being deposited again unchanged.

7. Trisodium phosphate takes up sulphur dioxide very readily; and alcohol separates sodium phosphate from the solution. If the crystals be saturated with sulphur dioxide, they form a solution which, on standing, separates into two distinct layers, which on being shaken unite to form a homogeneous liquid.

8. Bismuthic, stannous, stannic, and metastannic phosphates are in no way acted upon by sulphurous acid.

9. Silver, lead, and barium phosphates are acted upon by an aqueous solution of sulphurous acid in the same way as by other strong acids, so that sulphites and free phosphoric acid are formed.

10. Calcium arsenite, arseniate, and copper vanadate behave, with a solution of sulphurous acid, as the phosphates of the first class. The solution of calcium arsenite is decomposed by boiling into calcium sulphite; that of calcium arseniate slowly deposits calcium sulphate, formed at the expense of the oxygen of the arsenic acid; while that of copper vanadate, on boiling forms golden-yellow metallic-glancing scales, which appear to be vanadito-sulphite of copper.

11. Lastly, calcium oxalate is dissolved by sulphurous acid only to the very smallest amount, and undergoes no decomposition.

T. E. T.

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**On Silicon Hexbromide and Hexchloride.** By C. FRIEDEL  
(Compt. rend., lxxiii, 1011—1013).

In order to prepare the silicon hexbromide, a weighed quantity of silicon hexiodide is dissolved in carbonic disulphide, and bromine is

added in sufficient quantity to replace the iodine. The undissolved iodine is separated by filtration, and the dissolved iodine by shaking with mercury. The liquid on evaporation yields crystals of the silicon hexbromide; these crystals are doubly refractive, and can be distilled at about  $240^{\circ}$  without decomposition. On treatment with potash, hydrogen is evolved in the quantity required by the formula  $\text{Si}_2\text{Br}_6$ , that is,  $\text{H}_2$  for every equivalent of  $\text{Si}_2\text{Br}_6$ . The silicon hexchloride is obtained by gently heating the hexiodide with mercuric chloride; the formula is  $\text{Si}_2\text{Cl}_6$ , and it yields the corresponding quantity of hydrogen with potash. It is a colourless liquid, which crystallises about  $-1^{\circ}$ . Water decomposes it rapidly, furnishing a compound which is to a great extent soluble in the dilute hydrochloric acid formed; on adding ammonia, hydrogen is evolved, and a flocculent precipitate is formed.

A. P.

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**On the Passivity of Cadmium.** By SCHÖNN (Zeitschrift f. Anal. Chemie, x, 291—292).

THE author has already shown that nitric acid of sp. gr. 1.42 is rapidly decomposed by tin, but that this decomposition ceases when the metal is placed in contact with platinum. He has recently observed that cadmium behaves in a similar manner when placed in contact with platinum. Nitric acid of sp. gr. 1.47 is rapidly acted upon by cadmium under ordinary circumstances, but in contact with a sufficiently large surface of platinum the decomposition is arrested.

T. E. T.

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**Contributions to the Chemical History of Antimony.** By B. UNGER (Arch. Pharm. [23], cxlvii, 193—217, and cxlviii, 1—20).

*Sodium sulphantimonate*—Schlippe's salt— $\text{Na}_3\text{SbS}_4 + 9 \text{ aq.}$ , or  $3\text{Na}_2\text{S.Sb}_2\text{S}_5 + 18 \text{ aq.}$  The crystals of this salt effloresce in the air, and more quickly over sulphuric acid, giving off in the latter case 13 mols. water, and leaving the salt  $3\text{Na}_2\text{S.Sb}_2\text{S}_5 + 5 \text{ aq.}$

From his analysis of this salt, the author concludes that the atomic weight of antimony is 120.

*Sodium antimonate* differs in composition according to its mode of preparation. By precipitation of the product of the action of potash solution on antimony ore (antimony tersulphide) with soda solution, the well known compound  $\text{Na}_2\text{O.Sb}_2\text{O}_5 + 7\text{H}_2\text{O}$  is obtained.

a. By boiling the filtrate from this compound with sulphur,  $\text{Na}_2\text{O.Sb}_2\text{O}_5 + 6\text{H}_2\text{O}$  was obtained. b. By boiling antimony ore with potash-solution and sulphur, and precipitating with soda-solution,  $6\text{Na}_2\text{O}.5\text{Sb}_2\text{O}_5 + 38\text{H}_2\text{O}$  was formed. This salt is also produced when the hydrochloric acid solution of *sodium antimonate* (which separates from the mother liquors obtained in making Schlippe's salt) is treated with tartaric acid, diluted with water, and precipitated by soda solution in excess.

The solution of this salt scarcely alters the colour of litmus. The salt itself is difficultly soluble in pure water; a solution was obtained by long washing on the filter, containing in 100 grams 0.085 grm. of

salt. After ignition it yielded caustic soda on treatment with water, not however sufficient to leave the neutral salt  $\text{Na}_2\text{OSb}_2\text{O}_5$  as the residue.

*Crocus of antimony* is the well known lemon yellow body, formed when antimony tersulphide is treated with caustic alkaline solution. When dried at a gentle heat, it remains as an ochre-brown powder. Heated more strongly, it gives off water, and fuses, with intumescence, to a glassy mass, without any sublimation of  $\text{Sb}_2\text{S}_3$ , and has then the composition,  $3(\text{Sb}_2\text{S}_3 \cdot \text{H}_2\text{O}) + 6(\text{K}_2\text{O} \cdot \text{Sb}_2\text{O}_3) + 2\text{Sb}_2\text{O}_3$ .

It was not found possible to prepare the pure sodium compound, as insoluble antimoniate is formed, mixed with it, and cannot well be separated.

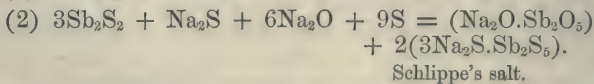
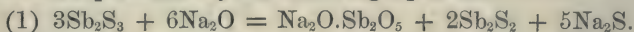
*Reactions of various antimony-compounds with sodium sulphide:—*

1. *Antimonious oxide* dissolves easily in sodium sulphide solution to a liquid of the colour of chlorine gas. Hydrochloric acid precipitates orange antimony tersulphide, without separation of sulphur.

2. *Sodium antimonate* dissolves but slowly in sodium sulphide solution, even with warming; in time, however, the solution takes up a large amount of it. From the almost colourless solution the *golden sulphide*,  $\text{Sb}_2\text{S}_5$ , is precipitated by acids, without admixture of free sulphur, showing that sulphantimonate of sodium has been formed.

3. When very finely pounded black antimony tersulphide and a little strong sodium sulphide solution were rubbed together, and warmed from  $20^\circ$  to  $30^\circ$ , a paste was formed, having a beautiful coppery lustre, and from this a body was obtained having almost the appearance of metallic copper, and the composition  $\text{Na}_2\text{Sb}_6\text{S}_{12} + 2\text{H}_2\text{O}$ , which the author represents by the formula  $\text{Na}_2\text{S} \cdot \text{Sb}_2\text{S}_5 \cdot 2\text{H}_2\text{O} + 3\text{Sb}_2\text{S}_2$ , supposing the body to contain a bisulphide of antimony analogous to realgar. When decomposed by an acid, however, it yields only the tersulphide. The mother-liquor of the copper-coloured body, treated with an additional quantity of sodium sulphide, yields a considerable quantity of Schlippe's salt.

When black antimony tersulphide is treated with potash-solution, and the liquid filtered from the resulting "crocus" is mixed with caustic soda, sodium antimonate is precipitated, and a liquid is obtained, which the author supposes to contain antimony bisulphide, dissolved in aqueous sodium sulphide. This liquid, treated with the necessary amount of sulphur, yields a further quantity of sodium antimonate, together with a considerable proportion of Schlippe's salt. The two reactions are represented by the following equations:—

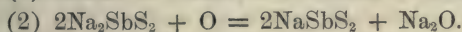
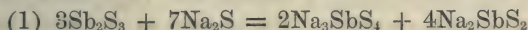


*Compound of Sulphantimonate and Hyposulphite of Sodium.*—By crystallisation of the red mother-liquors obtained in the preparation of Schlippe's salt, which contain much sodium hyposulphite, a new salt is obtained in large crystals, having the composition  $3\text{Na}_2\text{S} \cdot \text{Sb}_2\text{S}_5 + 2(\text{Na}_2\text{O} \cdot \text{S}_2\text{O}_2) + 40\text{H}_2\text{O}$ .



If the antimony ore from which the Schlippe's salt is obtained contains arsenic, the double salt will also be arsenical. This salt crystallises in a form different from that of Schlippe's salt, viz., in six-sided rhombic pyramids, very much like potassium sulphate. They have a faint greenish tint, effloresce, but not rapidly, and in time become opaque and brown. Treated with acids, they yield a mixture of golden sulphide with free sulphur, amounting to one-third of the weight of the whole precipitate. The saturated hot solution of this salt deposits first tetrahedrons of Schlippe's salt, and then sodium hyposulphite. The crystals melt when gently heated. This compound is of all known inorganic salts the one which contains the largest number of molecules of water.

4. The reaction of *antimony tersulphide* with sodium sulphide differs according to the relative quantities of the two bodies employed. When the tersulphide is treated with a small quantity of sodium sulphide in concentrated solution, the copper-coloured body already mentioned is formed, and in large quantity, if the ingredients are heated together for some time out of contact with the air. But when an excess of sodium sulphide is used, Schlippe's salt is formed, together with a red tarry body, which, by repeated solution in water and evaporation, may be obtained in deep red flocks, having the composition  $\text{NaSbS}_2$ , or  $\text{Na}_2\text{S} \cdot \text{Sb}_2\text{S}_3$ . The oxygen of the air is concerned in the reaction; for when the materials are placed together in a closed vessel, very little Schlippe's salt is formed. The author explains the result by supposing that a body having the composition  $\text{Na}_2\text{SbS}_2$ , or  $2\text{Na}_2\text{S} \cdot \text{Sb}_2\text{S}_2$ , is first formed, together with Schlippe's salt, and that the former is converted by oxidation into sodium sulphantimonite and caustic soda, thus:—



The precipitate produced when the solution of antimony tersulphide in sodium sulphide is poured into acids is very different from the beautiful penta- and ter-sulphides of antimony produced by the ordinary methods, being of the colour of iron oxide, or kermes: it is very bulky and gelatinous. It appears to be anhydrous, and when once dried, is scarcely at all hygroscopic.

This kermes-coloured precipitate possesses the peculiar property of persistently retaining from 1.5 to 2 p. c. sodium sulphide, in such a manner as to be difficultly decomposable by acids.

*Kermes*.—1 molecule of antimony tersulphide requires for complete solution 4 molecules of neutral potassium carbonate. The reaction may be represented by the equation  $3\text{Sb}_2\text{S}_3 + 12\text{K}_2\text{CO}_3 + 6\text{H}_2\text{O} = 2\text{KSbO}_3 + 2\text{Sb}_2\text{S}_2 + 5\text{K}_2\text{S} + 12(\text{KHCO}_3)$ .

In the filtrate from the kermes no free potassium sulphide could be detected by an alkaline lead-solution, but the reaction indicative of the presence of Schlippe's salt was obtained, showing that all the potassium sulphide present was in that form of combination.

Potassium sulphantimonate and potassium antimonate are found in the solution, the former resulting from the latter by the action of the

potassium sulphide, of which there is not sufficient to convert all the antimonate into sulphantimonate.

In conclusion, the author infers that the soluble compound formed of potassium sulphide and antimony bisulphide must have the composition  $K_2Sb_2''S_3$ , or  $K_2S.Sb_2S_2$ : for out of the 5 molecules of potassium sulphide (vide equation), 3 molecules are accounted for as going to form Schlippe's salt, leaving 2 molecules as the amount to unite with the 2 molecules of antimony bisulphide, and forming, not  $K_2SbS_2$  but  $K_2Sb_2S_3$ .

W. S.

### Compounds of Bismuth Oxide with Sulphuric Acid. By A. LEIST (Ann. Ch. Pharm. clx, 29—35).

HEINTZ\* obtained three bismuth compounds of sulphuric acid:—1. A basic salt,  $Bi_2O_3SO_3$ , by dissolving bismuth oxide in sulphuric acid, evaporating the solution to dryness, and carefully heating the residue till it became yellow. 2. A second basic salt,  $Bi_2O_3.2SO_3 + 3 aq.$ , was obtained by the addition of sulphuric acid to a solution of bismuth nitrate in nitric acid. 3. Salt 1, with water of crystallisation, by washing 2 with boiling water. A normal salt could not be obtained, except in combination with potassium, viz.,  $K_3Bi(SO_4)_3$ , which is thrown down as a crystalline precipitate on the addition of normal or acid potassium sulphate to a solution of bismuth nitrate, and Heintz expressed the opinion that a normal salt could not be prepared in the wet way. On the other hand, Schultz-Sellack† states that by dissolving bismuth oxide in moderately concentrated sulphuric acid, and evaporating, a normal salt,  $Bi_2O_3.3SO_3$ , is obtained in long, glistening, silky needles. The present experiments are a repetition of those of Schultz-Sellack, but do not confirm them. The author has obtained two salts crystallising in needles, the one an acid sulphate, the other Heintz's No. 2 salt, containing, however, one molecule of water less, possibly in consequence of its formation in presence of a larger proportion of sulphuric acid. Bismuth oxide is at first dissolved in considerable quantity by moderately concentrated acid (1 part acid to 2—3 parts water), but almost immediately afterwards a basic salt separates out, which is only re-dissolved by much hot acid of the above concentration (about one pound of concentrated acid was required to dissolve 15 grams of bismuth oxide). The solution may be filtered through paper. After evaporating until sulphuric acid fumes escape, and leaving the liquid to stand for 24 hours, the whole solidifies to a crystalline mass of long, silky needles, from which the excess of acid is removed by draining, first on a funnel stopped by coarse glass powder, and then on a dry brick, out of contact with moist air, and final pressing between filter paper.

These crystals are insoluble in water, but particularly soluble in hydrochloric and nitric acids. Treated with water, they lose sulphuric acid, and become more basic, but even after many days' washing, the wash-water still contains acid. Their composition is  $Bi_2O_3.4SO_3 +$

\* Pogg. Ann., lxi, 77.

† Deut. Chem. Ges. Ber., iv, 13.

7 aq., or  $\text{BiH}(\text{SO}_4)_2 + 3 \text{ aq.}$  The crystals from a second preparation, although containing the same relative amounts of  $\text{Bi}_2\text{O}_3$  and  $\text{SO}_3$ , gave numbers agreeing with the formula,  $\text{Bi}_2\text{O}_3 \cdot 4\text{SO}_3 + 9 \text{ aq.}$ , the probable explanation of this being that the two salts had separated out from acids of different degrees of concentration.

By dissolving the oxide in moderately concentrated acid, filtering hot, and evaporating until a considerable portion of the acid is driven off, the basic salt,  $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3 + 2 \text{ aq.}$ , begins to crystallise out, even from the hot solution in needles, which, however, are not so long as those of the above acid salt. They may be purified in a similar manner.

H. E. A.

### Preparation of Crystallised Chromium. By EMIL ZETTNOW (Pogg. Ann, cxlii, 477—479).

IN place of a mixture of chromic chloride with the chlorides of potassium and sodium, used by Wöhler in the preparation of chromium, Zettnow employs a double chloride of chromium and potassium. He forms this double salt from the red potassium chromate, by reducing it with hydrochloric acid, in presence of alcohol, and adding chloride of potassium to the boiling liquid, which is then evaporated to dryness. The residue, after being carefully dried, is mixed with finely granulated zinc, and this mixture is introduced by successive portions into a red-hot Hessian crucible, in which, after the last portion has been added, it is heated for half to three-quarters of an hour, and then allowed to cool slowly. The soluble salts are dissolved out by water, the zinc by dilute nitric acid.

C. C.

### Preparation of Pure Chromic Acid. By EMIL ZETTNOW (Pogg. Ann. cxliii, 468—474).

THE chromic acid prepared by the usual methods is far from pure, and requires a considerable quantity of the reagents. The decomposition of barium chromate by sulphuric acid gives a quantity of chromic acid, corresponding with the theoretical calculation, but the process is long and tedious, and requires great care.

The author gives an account of a series of experiments which he has made, in order to learn how to obtain chromic acid according to Traube's method (Ann. Ch. Pharm. lxvi, 8, 165), by the action of sulphuric acid on red potassium chromate, in a pure state, and with the most economical employment of the reagents.

To determine the proportion of the acid obtainable from the red chromate by this method, he heated 500 grams of the red chromate with 1250 c.c. of water, and 960 c.c. of sulphuric acid (of sp. gr. 1.83), and left the solution over night, during which time the acid sulphate of potash crystallised out. The mother-liquor was heated, mixed with



1100 c.c. of sulphuric acid, and then with water, till the precipitated chromic acid was re-dissolved. By evaporation of the solution till no more crystals formed, 301 grams of dried crystals of chromic acid were obtained (slightly impure by presence of potash and sulphuric acid), *i.e.*, 87.7 per cent. of the theoretical quantity. The smallest quantity of sulphuric acid (of sp. gr. 1.83) needed for the decomposition of 300 grams of red chromate was found to be 375 c.c., together with 500 c.c. of water.

The following is an account of the preparation of pure chromic acid:—

300 grams of pulverised commercial red potassium chromate are warmed with 500 c.c. of water, and 420 c.c. of sulphuric acid, until dissolved; the solution is allowed to stand for 10—12 hours, in which time the acid potassium sulphate crystallises out. The mother-liquor is decanted and allowed to drain for an hour or two, the salt being washed with 10—12 c.c. of water. The solution is heated to 80°—90°, mixed with 150 c.c. of sulphuric acid, afterwards gradually with the same quantity of water, until the precipitated chromic acid is re-dissolved. The solution is then evaporated until crystals begin to appear. After standing for 10 to 12 hours, the chromic acid is precipitated in small, brownish red crystals. The mother-liquor is decanted from the crystals, again evaporated, and allowed to stand; a second crop is obtained of rather larger feathery crystals, and in a similar manner a third of long, scarlet red needles. These crystals are freed from mother-liquor by draining in a funnel in the apex of which is a piece of thin platinum foil pierced with very small holes, and finally dried on a porous tile.

To purify the crystallised chromic acid thus obtained, it is introduced into a porcelain crucible, and treated gradually with 50 c.c. of pure nitric acid of sp. gr. 1.46 (weaker acid would dissolve the chromic acid), the mixture being thoroughly stirred with a glass rod; it is then conveyed to a dry tile. If, after standing thus for 12 hours, the chromic acid is found by testing to be not thoroughly freed from potash and sulphuric acid, it is sufficient to repeat the operation with 25 c.c. of the nitric acid to remove these impurities. The nitric acid is readily expelled from the crystals by heating on a sand-bath, first gently, then more strongly, until no more acid fumes are evolved.

By this method the author obtained an average of 84.8 p. c. of the theoretical quantity of pure and dry chromic acid. By using the green mother-liquor decanted after the third crystallisation, in place of fresh sulphuric acid, a considerable saving is effected, whilst the quantity of chromic acid thus procured is about 90.3 p. c. of the theoretical quantity, instead of 84.8 p. c.

C. C.

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**On the Specific Gravity of Pure Chromic Acid and of Chromic Acid Solutions.** By EMIL ZETTNOW (*Pogg. Ann.* cxliii, 474—477).

FOR the estimation of the specific gravity of solid chromic acid, the

author availed himself of commercial benzene, freed from water by digestion with calcium chloride. The dried benzene, whether hot or cold, does not dissolve the smallest quantity of chromic acid.

The sp. gr. of the solid chromic acid, as determined by six experiments, was 2·775, 2·777, 2·787, 2·785, 2·804, and 2·800 respectively, the mean being 2·788. Temp. 17·5° C.

*Specific gravity of Aqueous Chromic Acid.*

Percentage of CrO <sub>3</sub> dissolved.	Specific gravity of solution.	Percentage of CrO <sub>3</sub> dissolved.	Specific gravity of solution.
62·23 (saturated).	1·7023 at 26°	19·33.....	1·1569 at 19°
37·82 .....	1·34416 „ 22°	12·34.....	1·0957 „ 19·5°
	1·3448 „ 19·2°	8·79 .....	1·0694 „ 14·2°
32·59 .....	1·22384 „ 9·7°		1·0679 „ 18°
	1·22100 „ 15·2°	8·25 .....	1·0606 „ 16·2°
	1·21914 „ 18·6°		1·0600 „ 17°
	1·20940 „ 35°		
31·83 .....	1·20714 „ 12°		
	1·20264 „ 20·1°		
	1·20269 „ 20·9°		

C. C.

**On certain Chromium Compounds.** By JULIUS HEINTZE.  
(J. pr. Chem. [2] iv, 211).

A PRELIMINARY notice of these results has appeared in abstract, page 890 of the last volume. To the results thus briefly stated, the following may be added:—

Potassium chlorochromate is obtainable in long needles by dissolving the dichromate in three or four parts of warmed strong hydrochloric acid, and recrystallising the product from hot hydrochloric acid; it is partially decomposed by heat, and must be dried *in vacuo*. Dry, pure ammonia gas produces with the dry compound, ammonium chloride and a salt crystallisable from hot water, and having the formula CrO<sub>2</sub>.OK

CrO<sub>2</sub> ; its reactions seem to be identical with those of ordinary CrO<sub>2</sub>.OK chromates.

Ether and dry ammonia gas transform potassium chlorochromate into potassium amido-chromate CrO<sub>2</sub> {  $\begin{smallmatrix} \text{OK} \\ \text{NH}_2 \end{smallmatrix}$  }, crystallisable from water; cold caustic soda-solution does not decompose this body, but on boiling for some time ammonia is given off in quantity; on heating it with water to 100° for some hours, the following reaction takes place:—

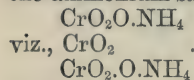


Similarly nitrous acid gives nitrogen, water, and potassium dichromate.

Neither platinum chloride, mercury chloride, nor silver nitrate combines with it.

Along with the amido chromate a body is formed giving numbers agreeing badly with the formula  $\text{Cr}_2\text{O}_3\text{NH}_2$ ; it is a chocolate-coloured powder insoluble in water, alcohol, ether, chloroform, and carbon disulphide. Acids and alkalis dissolve it on long heating, the latter with evolution of ammonia. The amount of this body formed is but small, but is increased by allowing the action of the ethereal ammonia to take place under a pressure of 1—2 decimetres of mercury.

Chromyl dichloride dissolves in glacial acetic acid and chloroform, without alteration; ammonia gas passed into the solution in the latter liquid produces a brown amorphous powder difficultly soluble in water, insoluble in alcohol, ether, chloroform, and glacial acetic acid, but readily soluble in acids, from which solutions it again separates as an amorphous powder. On analysis it yields numbers indicating that it is the ammonium salt corresponding to the potassium salt first described,



The trichromyl dichloride described by Thorpe,\* appears to be the  $\text{CrO}_2.\text{Cl}$  chloride corresponding to these salts, viz.,  $\text{CrO}_2$ .  
 $\text{CrO}_2.\text{Cl}$

By the action of strong hydrobromic acid on potassium dichromate solution, there is produced potassium bromochromate,  $\text{CrO}_2 \begin{Bmatrix} \text{OK} \\ \text{Br} \end{Bmatrix}$ , crystallisable from hot hydrobromic acid. This compound is less stable than the corresponding chlorochromate, losing bromine even at common temperatures.

Attempts to prepare potassium fluochromate have as yet given only chromium and potassium fluorides.

C. R. A. W.

**The Iridium Compounds analogous to the Combinations of Ethylene with Platinous Chloride.** By S. P. SADTLER (Am. J. of Sci. [3], ii, 338—344).

IN 1830, Zeise discovered and investigated a series of salts containing platinous chloride in combination with ethylene, to which compounds the general formula  $\text{PtCl}_2.\text{C}_2\text{H}_4 + \text{KCl}$  was assigned.

The very obvious analogy existing between platinum and iridium, suggested to the author the possibility of preparing a similar series of salts containing iridium in the place of platinum.

To carry out this investigation, it became necessary to prepare iridium perfectly free from platinum, and the method originally suggested by Birnbaum was eventually adopted, the separation being effected by converting both metals into their corresponding cyanides, combining the latter with barium, and then mechanically separating

\* Chemical News, 1869, 243.



the double cyanide of iridium and barium, from the double cyanide of platinum and barium.

To prepare the cyanides, a mixture of crude iridium oxide and potassium cyanide was fused in a small crucible, and maintained at a high temperature until all the metallic oxide was taken up. The fused mass when cold was dissolved in water, filtered from unattacked iridium oxide, and hydrochloric acid was added in sufficient quantity to destroy the excess of potassium cyanide. The liquid was then mixed with concentrated solution of copper sulphate; the violet-coloured precipitate, consisting of the mixed double cyanides of iridium and platinum with copper, was washed by decantation with boiling water; and while it was suspended therein, a strong solution of caustic baryta was added. The copper was thus precipitated as oxide, and the double cyanides of iridium and platinum with barium were formed. Carbonic anhydride was then passed through to precipitate the barium, and the solution concentrated to crystallisation.

The yellow platinum salt crystallised first, in small dichroic crystals, and afterwards the iridium salt in large colourless prisms, the crystallisation of both salts being so distinct and separate, that no difficulty whatever was encountered in their subsequent separation. The iridium crystals were ignited in a porcelain crucible, and the barium washed out with boiling water. The metallic iridium, after having been strongly ignited to effect its oxidation, was heated with aqua regia in a sealed tube to  $200^{\circ}$  to convert it into chloride; the latter was then treated with absolute alcohol, with addition of potassium or ammonium chloride, and the desired ethylene-salts obtained. The following decomposition takes place:—



Contrary to expectation, a simultaneous formation of several distinct ethylene-compounds resulted; in consequence of which, the analyses of the crystals do not prove so satisfactory as could be desired. The first preparation submitted to analysis gave the following results:—

	I.	II.
Iridium .....	33·5	—
Chlorine .....	35·92	35·65
Water .....	10·85	10·68

These percentages do not agree with the formula  $\text{IrCl}_2 \cdot \text{C}_2\text{H}_4 \cdot \text{KCl} + 2\text{H}_2\text{O}$ , which requires  $\text{Ir} = 48·45$ ;  $\text{Cl} = 26·19$  per cent.; moreover, the ratio of iridium to chlorine is 1—6. Upon the supposition, then, that the formula,  $\text{IrCl}_4(\text{C}_2\text{H}_4)_2(\text{KCl})_2 = x\text{H}_2\text{O}$ , is correct, we find as the theoretical percentage—

With $3\text{H}_2\text{O}$ .	With $2\text{H}_2\text{O}$ .	Anhydrous.
$\text{Ir} = 32·93$	$\text{Ir} = 33·95$	$\text{Ir} = 36·2$
$\text{Cl} = 35·61$	$\text{Cl} = 36·71$	$\text{Cl} = 39·14$
$\text{H}_2\text{O} = 9·03$		

The second sample was dried at  $100^{\circ}$ ; it yielded—

	I.	II.	III.
Iridium .....	37.21	34.26	—
Chlorine .....	41.59	—	39.53

When ammonium chloride was used in place of potassium chloride, a mixture of crystallised salts also resulted.

Preparation No. I agreed with the formula  $\text{IrCl}_2 \cdot \text{C}_2\text{H}_4 \cdot \text{NH}_4\text{Cl}$ , which requires 30.47 per cent. of chlorine.

	Experiment.	Theory.
Chlorine .....	30.74	30.47
Iridium (inaccurate)		

The second preparation differed in appearance from No. I, and corresponded with the formula  $\text{IrCl}_4(\text{C}_2\text{H}_4)_2(\text{NH}_4\text{Cl})_2$ .

	Experiment.	Theory.
Iridium .....	41.97	39.25
Chlorine .....	43.37	42.43

Two other samples of the ammonium salt examined appeared to consist of a mixture of the two above-mentioned salts in nearly equal proportions.

An attempt to substitute acetylene for ethylene in the foregoing compounds was unsuccessful.

J. W.

## Mineralogical Chemistry.

**Researches on Felspars.** By A. STRENG (Jahrbuch für Mineralogie, 1871, 598—619 and 715—731).

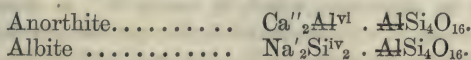
*Triclinic (sodio-calcic) Felspars.*—The author discusses the various observations that have been made on the chemical constitution and crystalline form of these minerals, and the views concerning them put forth by von Waltershausen, vom Rath, Tschermak, and Rammelsberg, and comes to the conclusion that all these felspars, viz., albite, oligoclase, andesin, labradorite, and anorthite, form an isomorphous group, the end terms of which are albite and anorthite, the former being a pure soda felspar, the latter a pure lime felspar, whilst the others are isomorphous mixtures of these two, approximating in physical properties and chemical composition to the one or the other accordingly as the soda or the lime predominates.

The composition of anorthite and albite may be represented as follows:—

Anorthite .....	$\text{Ca}''\text{Al}^{\text{vi}} \cdot \text{Ca}''\text{Al}^{\text{vi}} \cdot \text{Si}_4\text{O}_{16}$ .
Albite .....	$\text{Na}''_2\text{Al}^{\text{vi}} \cdot \text{Si}^{\text{iv}}_2 \cdot \text{Si}_4\text{O}_{16}$ .

the atomic group  $\text{CaAl}$  in anorthite being equivalent to the group  $\text{Na}_2\text{Al}$  in albite, and the second group  $\text{CaAl}$  in the former to  $\text{Si}_2$  in the latter.

The formulæ of the two minerals may also be written as follows :—



The general formula of a sodio-calcic felspar may then be written in the form  $\text{Na}_{2n}\text{Si}_{2n}\text{Ca}_{2-2n}\text{Al}_{1-n}\text{AlSi}_4\text{O}_{16}$ , in which  $n$  is a fraction intermediate between 0 and 1, whose denominator shows the number of molecules of albite which are present in the number of molecules of any other triclinic felspar denoted by the numerator.

These formulæ must not be looked upon as constitutional formulæ, but merely as indicating that equivalent groups  $\text{Ca}_2\text{Al}$ ,  $\text{Na}_2\text{Si}_2$ , play an analogous part in the two compounds. Analysis shows that the proportion of aluminium in a triclinic felspar increases with that of the calcium, and the proportion of silicon with that of the sodium.

The crystallographic differences between the three most important members of the series of sodio-calcic felspars, viz., albite, oligoclase, and anorthite, are shown in the following table, in which

$c$  denotes the principal axis.

A	the inclination of the axial planes	$ab, ac$	} in the right upper octant.
B	" "	$ab, bc$	
C	" "	$ac, bc$	
$\alpha$	the angle between the axes	$b, c$	
$\beta$	" "	$a, c$	
$\gamma$	" "	$a, b$	

*Albite.*

$a : b : c.$	A	B	C	$a$	$\beta$	$\gamma$
0.6284 : 1 : 0.5556	93°36'	116°18'	89°18'	94°22'	116°24'	87°26'

*Oligoclase from Vesuvius.*

0.6322 : 1 : 0.5525 | 93°28' | 116°13' | 91°36½' | 93°4½' | 116°23' | 90°4'

*Anorthite.*

$a : b : c.$	A	B	C	$a$	$\beta$	$\gamma$
0.6341 : 1 : 0.5501	94°10'	116°3'	92°34'	93°13'	115°55½'	91°12'

The values of A and B, as also those of  $a$  and  $\beta$ , are nearly the same in the three minerals, the chief differences lying in the values of C and  $\gamma$ . These differences, however, are not greater than those exhibited by many other isomorphous substances which are capable of crystallising together. It must be observed also that the magnitudes of the angles, and therefore also the ratios of the axes, are not constant, even for one and the same crystal, but vary with the temperature, and that bodies are comparable with one another, as regards their physical properties, not at the same temperatures, but at temperatures equally distant from their melting points, which differ greatly for the different felspars. When a triclinic crystal is heated, not only the angles of the faces, but likewise their parametric relations, are



altered, as also the angles of the axial planes and of the axes. If the angle of the axes *ab* in oligoclase, which is nearly  $90^\circ$ , is altered in either direction by heating, it will be altered in the opposite manner on cooling, the angle in question becoming in the one case more acute, and causing the form of the crystal to approximate to that of albite, while in the other case it will become more obtuse, and nearer to that of anorthite.

Lastly, the mode of formation of its twin crystals shows that oligoclase is intermediate between albite and anorthite. In anorthite the axis of combination is parallel to the macrodiagonal; in albite it is perpendicular to the brachydiagonal; while in oligoclase it is sometimes in the first direction, sometimes in the second.

*Albite and Orthoclase from Harzburg.*—These two minerals occur in the graphic granite of the Radauthal, near Harzburg. The albite is found—1. Crystallised in druses, mostly implanted on orthoclase in parallel rows. 2. Imbedded in the orthoclase in distinct layers, partly parallel to  $oP$ , partly to  $\infty P\infty$ . 3. Intergrown with orthoclase in lamellæ, recognisable only by the microscope, the lamellæ being partly parallel to  $\infty P\infty$ , partly to  $\infty P\infty$ . 4. As an independent constituent of the graphic granite, but in this case also intergrown with small quantities of orthoclase. Thin slices of both minerals when examined by the microscope, are seen to be interspersed with very minute blue or greyish-blue granular, and extremely thin brown-red lamellæ of some foreign mineral or minerals. The lamellæ probably consist of iron-glance or mica.

The albite crystals are mostly twins, having their axis of combination perpendicular to the brachypinacoid  $\infty P\infty$ , very rarely parallel to the principal axis. Simple crystals are, however, also found, not exhibiting any re-entering or projecting edges. The crystals are mostly combinations of the faces  $\infty P'_1$ ,  $\infty P_1$ ,  $\infty P_3$ ,  $\infty P'_3$ ,  $oP$ ,  $\infty P\infty$ ,  $2P\infty$  (occurring as a truncation of the acute edge  $oP'_1 : \infty P\infty$ ),  $P_1\infty$ ,  $2P_1\infty$ , and  $P_1$ .

The faces  $oP$  and  $\infty P\infty$  are mostly predominant, the prismatic faces subordinate, sometimes, however, equally developed with the other faces. The eight prismatic faces are never present altogether. The crystals are white to colourless, have a strong lustre, and are translucent to transparent. Sp. gr. =  $2.609$  at  $12^\circ$ .

The analysis of this albite showed that it is a mixture 20 mol. pure albite (sodic felspar), and 1 mol. anorthite (calcic felspar), or 94.85 p. c. albite and 5.15 anorthite.

	Calc.	Found.		Calc.	Found.
SiO <sub>2</sub> ....	67.40	67.75	Or: Si .....	31.69	31.86
Al <sub>2</sub> O <sub>3</sub> ....	20.43	18.42	Al .....	10.92	9.85
Fe <sub>2</sub> O <sub>3</sub> ....	—	2.08	Fe .....	—	1.52
CaO ....	1.03	0.92	Ca .....	0.74	0.66
MgO ....	—	0.14	Mg ....	—	0.08
K <sub>2</sub> O ....	—	0.38	K .....	—	0.32
Na <sub>2</sub> O ....	11.14	11.81	Na .....	8.26	8.76
	<hr/> 100.00	<hr/> 100.00			

The orthoclase occurs in drusy cavities of the graphic granite, in crystals from 1 to 2 inches long, and of simple form, exhibiting mostly only the prismatic face  $\infty P$  and the three pinacoids.  $\bar{P}\infty$  is rarely visible. The mineral is greyish white, opaque and dull. Analysis gave—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.
65·21	20·40	1·04	0·55	0·06	9·27	4·77 = 101·40

Or,	Si.	Al.	Fe.	Ca.	Mg.	K.	Na.	O.
	30·66	10·91	0·81	0·39	0·04	7·78	3·54	47·37 = 101·40

These numbers give—

$$R''R'_2 : R^v : Si = 1 : 1·15 : 5·84.$$

showing that the orthoclase in question is very impure, since for pure orthoclase the ratio is 1 : 1 : 6. If the impurities be regarded as iron-glance, and the iron be accordingly left out, the ratio becomes 1 : 1·07 : 5·84, which does not differ much from that of pure orthoclase. The ratio of the alkalis and alkaline earths shows that the mineral is a mixture of about 6 molecules of pure orthoclase with 5 molecules of a sodio-calcic felspar, containing but a small proportion of calcium.

The mineral from the graphic granite of the Radauthal described by Fuchs (Leonhr. Jahrb. 1862, 789) as oligoclase, and containing 65·83 p. c. SiO<sub>2</sub>, 20·46 Al<sub>2</sub>O<sub>3</sub> with a trace of Fe<sub>2</sub>O<sub>3</sub>, 0·71 CaO, with trace of MgO, 6·94 K<sub>2</sub>O and 5·89 Na<sub>2</sub>O, appears rather to be an albite rich in potash, since the proportion of lime is much too small for oligoclase.

Orthoclase from Elba, in which G. vom Rath found 3·40 p. c. Na<sub>2</sub>O to 11·93 K<sub>2</sub>O was also found by Streng, on microscopic examination, to be intersected by lamellæ and small crystals of albite.

H. W.

**The Crystalline System of Humite.** By G. vom RATH (Pogg. Ann. Ergänzungsband, v, 320—413, Jahrbuch f. Min., 1871, 634).

THE author's observations confirm the discovery of Scacchi, that the crystals of this mineral are referrible to a three-fold type. The numerous combination-faces might indeed be all referred to one primary form; and if we select for this form a pyramid of any one of the three groups or types, then all faces occurring on the same crystal, or on crystals of the same group, may be represented by simple indices; but if the same pyramid be chosen as the primary form of the crystals of the other two groups, the numerous combination-forms of these crystals will be represented by very complicated indices, although they stand to one another in very simple relations, as above observed, with respect to the forms belonging to one and the same group. Nevertheless, the difference between the three primary forms to which the crystals of the three groups must be referred, in order that their combinations may be represented by simple numbers, relate to only one axis, that is to say, to the ratio of this axis to the other two, whereas

the lengths of these latter bear the same ratios to one another in all the three groups.

Type I. Calling the macrodiagonal  $a$ , the brachydiagonal  $b$ , and the principal axis  $c$ , the ratios of the axes are :

$$a : b : c = 1.08028 : 1 : 4.40131.$$

The observed forms are :

Pyramids of the principal series..	$P, \frac{1}{2}P, \frac{1}{3}P.$
Macropyramids.....	$\bar{P}2, \frac{1}{2}\bar{P}2, \frac{1}{3}\bar{P}2, \frac{1}{4}\bar{P}2, \frac{1}{5}\bar{P}2.$
Prisms .....	$\infty P, \infty \bar{P}2, \infty \bar{P}\frac{3}{2}.$
Brachydomes .....	$\bar{P}\infty, \frac{1}{2}\bar{P}\infty, \frac{1}{4}\bar{P}\infty, \frac{1}{3}\bar{P}\infty, \frac{1}{5}\bar{P}\infty.$
Macrodomes .....	$\bar{P}\infty, \frac{1}{3}\bar{P}\infty, \frac{1}{5}\bar{P}\infty.$
Pinacoids .....	$0P, \infty \bar{P}\infty, \infty \bar{P}\infty.$

Twins occur: (1), with  $\frac{3}{7}\bar{P}\infty$  as contact-plane; (2), with  $\frac{1}{7}\bar{P}\infty$ . The crystals of the first type are mostly simple; but there are also very regular twins, and, on the other hand, very irregular triple crystals. Cleavage distinctly basal. Colour white, yellowish-white, honey-yellow, chestnut-brown, brown. With the dichroscope, differences of colour are scarcely perceptible; the same also is the case in the other two types.

Type II.  $a : b : c = 1.08028 : 1 : 3.14379$ . Whilst the crystalline forms of the first type are invariably holohedral, those of the second exhibit a peculiar and remarkable hemihedry, which converts a portion of the pyramids into hemipyramids. In consequence of this, the crystals of the second type acquire an apparent monoclinic development, whilst the axial elements remain rhombic. The observed forms of this type are :

Pyramids of the principal series..	$P, \frac{1}{3}P.$
Macropyramids.....	$2\bar{P}2, \frac{2}{3}\bar{P}2, \frac{2}{5}\bar{P}2, \frac{2}{7}\bar{P}2.$
Brachypyramids .....	$3\bar{P}\frac{3}{2}, \frac{3}{5}\bar{P}\frac{3}{2}.$
Brachydomes .....	$\bar{P}\infty, \frac{2}{5}\bar{P}\infty, \frac{1}{3}\bar{P}\infty.$
Macrodomes .....	$\frac{1}{2}\bar{P}\infty, \frac{1}{4}\bar{P}\infty.$
Pinacoids .....	$0P, \infty \bar{P}\infty.$

Twins: (1) with  $\frac{1}{3}\bar{P}\infty$  as contact-plane; (2), with  $\frac{2}{5}\bar{P}\infty$ . Colour light to dark yellow. The crystals of this type are more interesting than those of the other two, on account of the great variety of their forms; but a searching investigation is often required, not only for the determination of their type, but even of their relation to humite in general.

Type III.  $a : b : c = 1.08028 : 1 : 5.65883$ . These numbers, compared with the preceding, show that, with equal secondary axes, the principal axes of the first, second, and third types are to one another as 7 : 5 : 9. This third type includes by far the greatest number of humite crystals; and these crystals are not only the most complicated of the humite species, but likewise the most numerous faced of all known minerals. Hemihedry prevails in this as in the second type; but whereas in the latter the pyramid of the principal series is hemi-



hedrally developed, the corresponding pyramids of the third type are holohedral, and the hemihedry occurs in the macro- and brachy-pyramids. The observed forms are:

Pyramids of the principal series..	$P, \frac{1}{3}P, \frac{1}{5}P, \frac{1}{7}P.$
Macropyramids.....	$2\bar{P}2, \frac{2}{3}\bar{P}2, \frac{2}{7}\bar{P}2, \frac{2}{9}\bar{P}2.$ $\frac{2}{11}\bar{P}2, \frac{2}{13}\bar{P}2, \frac{2}{15}\bar{P}2, \frac{2}{17}\bar{P}2.$
Brachypyramids .....	$3\bar{P}\frac{3}{2}, \bar{P}\frac{3}{2}, \frac{1}{3}\bar{P}\frac{3}{2}.$
Brachydomes .....	$\bar{P}\infty, \frac{1}{3}\bar{P}\infty, \frac{1}{5}\bar{P}\infty, \frac{1}{7}\bar{P}\infty, \frac{1}{9}\bar{P}\infty.$
Macrodomes .....	$\frac{1}{2}\bar{P}\infty, \frac{1}{4}\bar{P}\infty, \frac{1}{6}\bar{P}\infty.$
Pinacoids .....	$0P, \infty\bar{P}\infty, \infty\bar{P}\infty.$

Twins occur with  $\frac{1}{3}\bar{P}\infty$  as contact-plane. The colour is mostly brown of various shades, but also yellow, yellowish-white, and white. The colour appears to afford no criterion for the determination of the type. Humite of the third type has hitherto been seldom found together with the first, and never with the second. Its crystals occur especially in two rock-formations, viz., in granular limestone, or in an aggregate of green augite with mica and subordinate separations of lime.

The number of faces observed in humite, including the three pinacoids, and counting the faces common to two types only once, amounts to 135.

The chemical constitution of humite varies to a certain extent with the difference of type. The general formula of the magnesium silicate in humite is  $Mg_3Si_3O_{14}$  or  $8MgO.3SiO_2$ , the oxygen being more or less replaced by fluorine, and in such proportion that the principal axis of the primary form diminishes in length as the proportion of fluorine increases, thus:

Third type.....	$Mg_{48}Si_{18}O_{88}F_4.$
First „ .....	$Mg_{48}Si_{18}O_{81}F_6.$
Second „ .....	$Mg_{48}Si_{18}O_{80}F_8.$

The question, whether olivine, which exhibits a similar composition, belongs to one of the three types of humite, must, in vom Rath's opinion, be answered in the negative, inasmuch as the two minerals do not exhibit the intimate relation resulting from isomorphism. That the chondrodite of Pargas belongs to the second humite type has been shown by N. v. Kokscharow (Jahrb. f. Min. 1870, 783). A more exact investigation of the chondrodite of other localities would be of especial interest, since the second type is the rarest on Vesuvius, and therefore it is scarcely to be expected that this type should be the only one occurring in the contact-layers of the north.

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**On Obtuse Rhombohedrons and Hemiscalenohedrons on the Crystals of Quartz from Striegau in Silesia.** By WEBSKY (Jahrb. f. Mineralogie. 1871. 732—742).

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**Crystallographical Notices:**—Apatite, from Corbassera, Botteno, and Baveno: by J. STRÜVER.—Pyrite, from Meana and from Pesey: by J. STRÜVER.—Gmelinite: by H. GÜTHE.—Crystals of Heavy Spar from Vialas: by J. STRÜVER.—Magnetic Iron Ore from Traversalla: by J. STRÜVER.—Azorite and Pyrite, from St. Miguel: by A. SCHRAUF (Jahrb. für Mineralogie, 1871, 751—754).

**Analysis of Idocrase from Arendal in Norway.** By  
A. DAMOUR (Comptes rendus, lxxiii, 1040).

THE mineral in question, which is that known as olophonite, consists of rounded, translucent, yellowish grains, distributed throughout a calcareous matrix. Its specific gravity = 3.44. It is harder than felspar, fusible in the blowpipe flame, and readily acted upon by acids. It contains in 100 parts—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	FeO.	MnO.	MgO.	H <sub>2</sub> O.
36.32	16.70	34.86	6.20	1.40	0.73	2.58 = 98.79

The above composition, expressed by the formula  $18(\text{CaO}, \text{FeO}, \text{MnO}, \text{MgO}) + 4\text{Al}_2\text{O}_3 + 15\text{SiO}_2$ , agrees with the formula which has been recently assigned to idocrase, with which latter mineral the specimen also corresponded in its artificial and other physical characters.

*Analysis of a Mexican Garnet.*—The foregoing mineral having been frequently classed among the garnets, the author supplements the communication by appending the analysis of a garnet, the origin of which he was acquainted with. The specimen was obtained from a locality, Rancho de San Juan, where a crystalline limestone is the prevailing rock. The sample was crystalline, and of a pale, rose-red colour; hardness, greater than that of quartz; sp. gr. = 3.57. When fused in the reducing flame with borax, it yielded a colourless glass. The garnet was slowly acted upon by acids, but was more readily dissolved when it had been previously ignited to redness in a platinum crucible. It gave the following percentage, which is that of a grossular garnet:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MnO.	MgO.	Volatile matter.
39.46	21.69	1.36	35.75	0.96	0.67	0.40 = 100.29

J. W.

**On the Occurrence and Mode of Formation of the Phosphorite found on the Dniester, in Russian Podolia, Galicia, and Buckowina.** By F. SCHWACKHÖFER (Wien. Akad. Ber., lxxiii [2], 809—835).

IN this paper the author gives the results of his examination of the phosphatic deposits of the Dniester, undertaken at the request of the Austrian Minister of Agriculture. The following is a summary of his results:—

*Mineralogical Character.*—The Podolian phosphorite is essentially concretionary in its formation; in form nodular, the exterior being of a dark, cast-iron grey colour, and soapy to the touch. Where the

nodules have been much acted upon by attrition and weathering, their colour is often reddish brown, due to oxidation of the iron in them. They vary in weight from 4 to 500 grams. The powdered nodules when heated give out a phosphorescent light. There is generally found in the centre the originating nucleus of deposit, such nucleus being of Iceland spar, or of a brown, earthy substance. Inclosed in different parts of these concretionary nodules are found other mineral substances, such as calcite, quartzite, oxide of iron, oxide of manganese, &c. Lead glance is occasionally met with.

*Geological Occurrence.*—These phosphatic deposits are found in the Silurian schistose rocks of the Dniester basin, and in the eastern portion of Galicia. The chalk there rests unconformably on the Silurian schists, the intermediate formations being absent. Though these deposits are mainly found in the thin and friable schistose shales from which they have originated, they are also found in the younger rocks, which rest unconformably on the Silurian schists. As these rocks—overhanging the Dniester—break up through weathering agencies, it often happens that the nodules are found far distant from their original matrix bed, owing to the action of the river on the detached rocks. The chief deposits occur on the left bank of the Dniester, between St. Ushzica and Mogilew, and in the valleys running into the Dniester. The finest example of exposed deposits is near Zurczewka, Kaljus, and Ljadowa. It appears that they occur only where the chalk-marl lies on the schist; where other rocks intervene, or where the chalk is absent, no deposits have been found.

*Mode of Formation.*—It appears from the author's chemical and physical examination of these nodules, that they were originally composed of calcium carbonate, which has been gradually changed to phosphate by infiltration. The action of surface-water on the marls has produced the nodules of calcium carbonate found in the underlying schists. The author enters at some length into this question of the more or less complete transformation of the original nodules of calcium carbonate into phosphate. In support of his view he adduces the fact that he has found such nodules of calcium carbonate in various stages of formation. In many instances they consist entirely of calcium carbonate of a shell-like concretionary character. That these chalk concretions have been acted on by water containing phosphoric acid in solution, obtained from the phosphate-bearing schistose rocks, the author deems to be abundantly proved by the fact that most of the other constituents of these rocks are found in the altered chalk nodules.

To prove this action of phosphoric acid on calcium carbonate, the following experiments were made:—

A small ball of marble,  $1\frac{1}{2}$  c.m. in diameter, was placed in a solution of sodium phosphate for 14 days, at the ordinary temperature. The nodule was then removed, finely ground, and thoroughly washed with water. The well-washed powder gave distinct evidence of phosphoric acid when treated with ammonium-nitro-molybdate. The clear sodium phosphate solution, after removal of the marble, gave on boiling a deposit of basic calcium phosphate. This reaction being established, the author next made the following quantitative experiments:—





SiO <sub>2</sub> .....	42·965	3CaO.P <sub>2</sub> O <sub>5</sub> ....	32·950	} 38·359 phosphorite.
Fe <sub>2</sub> O <sub>3</sub> .....	3·575	CaF <sub>2</sub> .....	3·535	
Al <sub>2</sub> O <sub>3</sub> .....	5·814	Al <sub>2</sub> O <sub>3</sub> .P <sub>2</sub> O <sub>5</sub> ....	1·874	} 5·449 Dolomite or siderite.
CaO .....	20·895	MgO.CO <sub>2</sub> .....	1·602	
MgO.....	0·763	FeO.CO <sub>2</sub> .....	3·847	}
K <sub>2</sub> O .....	0·751	Fe <sub>2</sub> O <sub>3</sub> .....	0·922	
Na <sub>2</sub> O.....	0·593	Al <sub>2</sub> O <sub>3</sub> .....	5·027	}
P <sub>2</sub> O <sub>5</sub> .....	16·180	K <sub>2</sub> O .....	0·751	
CO <sub>2</sub> .....	2·298	Na <sub>2</sub> O .....	0·593	} 55·946 glauconite, alunite, and quartz.
SO <sub>3</sub> .....	0·076	SO <sub>3</sub> .....	0·076	
F.....	1·722	SiO <sub>2</sub> .....	42·965	}
Basic water and organic matter.....	4·702	Basic water and organic matter.....	4·702	
Hygr. water....	0·910	Hygr. water....	0·910	}
<hr/> 101·244		<hr/> 99·754		

From this it appears that the phosphorite sandstone of Grodno corresponds to most of the Russian phosphorite formations to the east of Grodno, but belongs to the upper chalk-formation.

H. W.

**The so called "Steel-ore" or "Codorus ore" of Pennsylvania.** By S. MARTIN (Proc. of the Lyceum of Nat. Hist. of New York, i, 51, 61; Jahrb. f. Min., 1871, 756).

THIS ore, used in large quantities in the blast-furnaces of York, Pennsylvania, for the manufacture of cast-steel, resembles a mica-slate, interspersed throughout with dark crystalline grains. It contains about 40 p. c. magnetic iron-ore, and 10 p. c. ferric oxide. Chromium has also been detected in it, but is mostly free from sulphur and phosphorous. In some specimens, however, cobaltiferous pyrites and brochantite have been found, together with magnetic iron-oxide, also some zinc and lead, together with incrustations of allophane.

H. W.

**The Dolomitic Springs of the Jura.** By E. v. GORUP-BESANEZ (Ann. Chem. Pharm. Suppl. Band viii, 230—242).

THE author refers to the fact that many so-called dolomites do not, upon analysis, give numbers expressing the relative amounts of calcium and magnesium carbonates corresponding to the numbers required by the formula  $\text{CaCO}_3 + \text{MgCO}_3$ , viz.,  $\text{CaCO}_3$  54·34 and  $\text{MgCO}_3$  45·66 per cent.

G. Bischof considers that mixtures of calcium and magnesium carbonates containing calcspar crystals, are but in the process of forming dolomite, while those with crystals of magnesite are perfectly formed dolomites. According to Bischof, from a solution of the former of these, calcium carbonate crystallises out; while from the true dolomites magnesite is dissolved out by water, and may be obtained as such from the solution.

The author gives analyses of a number of springs rising in the valleys of the Jura. Silica, calcium carbonate, and magnesium carbonate are the only important ingredients of these waters; chlorine, iron, and alkalis, together with bituminous organic matter, occur also in minute quantities.

A great many of the wells are pure dolomite springs, the percentage amounts of calcium and magnesium carbonates agreeing closely with those of dolomites occurring in the neighbourhood, and analysed by the author; these gave  $\left\{ \begin{array}{l} \text{CaCO}_3 \text{ } 57\cdot32 \\ \text{,,} \text{ } 57\cdot21 \end{array} \right.$  and  $\left\{ \begin{array}{l} \text{MgCO}_3 \text{ } 42\cdot68 \\ \text{,,} \text{ } 42\cdot79 \end{array} \right.$  while the mean of the water-analyses gave  $\text{CaCO}_3 \text{ } 53\cdot71$ , and  $\text{MgCO}_3 \text{ } 14\cdot29$ .

Some of the waters, however, differed widely from these numbers, showing as much as 88 per cent. and 89 per cent.  $\text{CaCO}_3$  to 12 per cent. and 11 per cent.  $\text{MgCO}_3$  in two instances; and 70 per cent. and 68 per cent.  $\text{CaCO}_3$  to 30 per cent. and 32 per cent.  $\text{MgCO}_3$  in the case of two other springs.

As those wells which occur where there is abundance of true dolomite formation, are shown to have the composition of true dolomite waters, the author is led to regard Bischof's view—that water containing carbonic acid dissolves dolomite in fixed proportions, from which solution it may again be obtained without decomposition—as correct. This he further corroborates by experiments on the amounts of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  taken up from dolomite by carbonated water in 5—8 and 21 days.

The author shows, however, by experiments, that, although carbonated water takes up fixed relative quantities of  $\text{CaCO}_3$  and  $\text{MgCO}_3$ , from what Bischof calls perfectly formed dolomites, yet, on evaporation, a large quantity of the  $\text{CaCO}_3$  is first thrown down, and the  $\text{MgCO}_3$  only after long evaporation. From this and other reasons the author thinks that carbonated water takes up fixed relative quantities of calcium and magnesium carbonates, as well from Bischof's imperfect as from perfect dolomites; and since from a solution of neither of these is crystalline magnesite ever deposited on evaporation, he regards as incorrect Bischof's view, that the presence of magnesite proves that the dolomite in which this occurs is a perfectly formed one. The geological formation of dolomites is as yet unsettled, but the author's experiments are opposed to Bischof's theory, viz., that from magnesian limestones carbonated water dissolves out only calcium carbonate, until the molecular proportion of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  in a perfect dolomite is obtained.

T. E. T.

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**Acidulous Chalybeate Water from Melrose.** By JAMES DEWAR  
(Chem. News, xxiv, 171).

THE composition of this water in grains per gallon is—

$\text{FeCO}_3$ .	$\text{Al}_2\text{O}_3$ .	$\text{SiO}_2$ .	$\text{MgSO}_4$ .	$\text{CaCl}_2$ .	$\text{CaCO}_3$ .	Alkaline chlorides.
17·5	1·8	8·5	7·8	16·0	4·1	11·4 = 78·1



This water appears to be the richest chalybeate in Great Britain, with the exception of "Muspratt's chalybeate," at Harrogate, which contains 10·8 grains per gallon of ferrous carbonate and 16·0 of ferrous chloride.

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## Organic Chemistry.

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**On a Hexyl Alcohol from the Essential Oil of Heracleum.** By A. FRANCHIMONT and TH. ZINCKE (Deut. Chem. Ges. Ber. iv, 822—825).

Two years ago Zincke (Ann. Ch. Pharm. clii, 1) found that the oil of the indigenous *Heracleum* species contains primary octyl alcohol in combination with acetic and caproic acids. The same alcohol was found in foreign species, together with another alcohol, probably a hexyl alcohol, which was obtained in quantities too small for a complete examination. The authors have re-commenced this research, Dr. Hugo Müller placing at their disposal 200 grams of the oil of *Heracleum giganteum*, which was prepared in London. The greater part of this oil, which distilled between 201°—206°, was found to be a mixture of hexyl butyrate (the butyric acid being the normal one) and of octyl acetate. The two alcohols were isolated by saponifying the oil with alcoholic potash, and separated by fractional distillation.

The *hexyl alcohol* thus obtained is a colourless oily liquid with a strong aromatic odour. Its specific gravity at 23° = 0·819, and the corrected boiling point 156·6°. The corresponding *hexyl iodide*,  $C_6H_{13}I$ , is a colourless liquid with a faint odour: specific gravity at 17·5° = 1·4115, boiling point 179·5°.

The *acetate*,  $C_6H_{13}.C_2H_3O_2$ , is a colourless, oily liquid, having at 17·5 the specific gravity 0·889, and boiling at 168·7°. The *caproate*,  $C_6H_{13}.C_6H_{11}O_2$ , is an oily liquid with hardly any smell. Specific gravity at 17·5° = 0·865; boiling point 245·6°.

On oxidation, this alcohol yields caproic acid, which boils at 204·5°—205°, and has, therefore, the same boiling point as Lieben's normal caproic acid. As this hexyl alcohol boils higher than all other primary hexyl alcohols so far studied, and as the difference between its boiling point and that of Lieben's normal amyl alcohol is 19°, it appears most probable that it represents the normal hexyl alcohol.

C. S.

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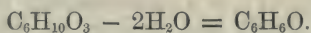
**Phenol from Glycerin.** By ED. LINNEMANN and V. VON ZOTTA. (Ann. Chem. Pharm., Suppl. viii, 254—260.)

On heating glycerin with chloride of calcium, a number of products are formed, amongst which are acrolein, propyl aldehyde, acetone, and allyl alcohol, and a liquid boiling between 180°—190°. Of the latter, about one-third dissolves in a concentrated solution of potash; on distilling the alkaline solution with dilute sulphuric acid, a distillate is

obtained possessing all the properties of a concentrated solution of phenol. On adding potassium carbonate to this solution, the phenol separated out as an oil, boiling between  $180^{\circ}$ — $190^{\circ}$ . Although 3000 grams of glycerin had been used, the quantity of the phenol obtained was too small to obtain it in the pure state, but its identity with coal tar phenol was proved by the odour, by the characteristic coloration which it gave with bleaching powder, and by converting it into picric acid. The potassium salt of this acid contained 14.93 per cent. K, the quantity calculated for potassium picrate being 14.64 per cent.

Small quantities of phenol are also formed by the action of zinc-chloride and potassium bisulphate upon glycerin, but not upon acrolein.

The liquid insoluble in caustic potash is *glycerin-ether*,  $C_6H_{10}O_3$ ; it is a somewhat thick colourless liquid, smelling like spearmint, and almost completely soluble in 20 parts of water. On heating it with water for four hours to  $160^{\circ}$ , it is converted into glycerin. By heating it gently with dilute hydrochloric or sulphuric acid, or a little zinc-chloride, a strong odour of aldehyde is developed, and the distillate reduces an ammoniacal silver-solution. On heating it with a concentrated solution of potash, phenol is formed, besides volatile acids. This so-called glycerin-ether has very great resemblance to the *monallylin*  $C_6H_{12}O_3$ , which Tollens obtained as a bye-product in the preparation of allyl alcohol from glycerin and oxalic acid. From the following experiments it appears that the two compounds are identical. On heating monallylin with water to  $160^{\circ}$ , only glycerin is formed, and by distilling it with dilute acids or zinc-chloride, an aldehyde is formed, besides a little acrolein. The aqueous distillate was treated with silver oxide, and thus a silver-salt obtained, containing 60.15 per cent. of silver, from which it would appear that the aldehyde is propyl aldehyde. The formation of phenol from glycerin-ether may be explained by the following equation:—



C. S.

**On an Isomeric Chloronitrophenol.** By AUG. FAUST. (Zeitschr. f. Chem. [2] vii, 338.)

A MIXTURE of equal weights of phenol and sulphuric acid was heated for some hours in a water-bath, diluted with water to a thin syrup, saturated with chlorine, and then poured into nitric acid, of sp. gr. 1.33. The mixture of chloronitrophenols so obtained was converted into potassium salts, and these were separated by crystallisation.

The author's expectation was, that if three phenolsulphonic acids were formed by the action of sulphuric acid on phenol, three isomeric dichloronitrophenols would be obtained on nitration. His product contained only two, namely, Fischer's, melting at  $121^{\circ}.5$  and Seifert's, melting at  $125^{\circ}$ , the latter in small quantity only. Besides these he obtained  $\beta$ -dinitrochlorophenol, melting point  $111^{\circ}$ , in considerable quantity. He also found this latter to be formed by chlorination of dinitrophenol, and also by the action of hydrogen chloride on diazo-dinitrophenol (from picramic acid).

This  $\beta$ -dinitrochlorophenol was reduced by ammonium sulphide, forming  $\beta$ -amidonitrochlorophenol,  $C_6H_2NH_2NO_2ClOH$ , of which the hydrochloride, sulphate, and barium-derivative were prepared.

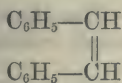
$\beta$ -nitrochlorophenol,  $C_6H_3NO_2ClOH$ , was obtained from the  $\beta$ -amidonitrochlorophenol by Gries's method. It forms, when crystallised from hot water, milk-white, silky, glistening needles, which melt at  $111^\circ$ . It is very soluble in ether, chloroform, and alcohol, but does not crystallise well from these solvents. *Potassium-derivative*,  $C_6H_3NO_2ClOK + aq.$ : short brown needles, very soluble in water. *Barium-derivative*,  $(C_6H_3NO_2ClO)_2Ba + 7aq.$ : yellow soluble needles. *Silver-derivative*,  $C_6H_3NO_2ClOAg$ : fan-like groups of copper-brown needles, difficultly soluble in water.  $\beta$ -amidochlorophenol,  $C_6H_3NH_2ClOH$ , is obtained by reduction with tin and hydrochloric acid. The hydrochloride forms yellowish very soluble plates.

H. E. A.

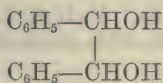
**Contributions to the History of the Benzoic Series.** By TH. ZINCKE. (Deut. Chem. Ges. Ber., iv, 836.)

THE author enters into discussion of the various constitutional formulæ proposed by Limpricht, Staedler, Jena, Grimaux, and Kekulé for bodies of this series. He then describes oxidation experiments with stilbene, benzoïn, and benzile, undertaken in the hope of throwing further light on the subject.

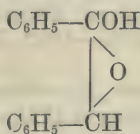
Stilbene yields benzoic aldehyde and benzoic acid on oxidation; all experiments to oxidise it completely to benzoic aldehyde were unsuccessful, benzoic acid being always formed at the same time. Benzoïn gives the same products. Benzile is somewhat less readily oxidised than either of the above, but on continued heating is finally resolved into benzoic acid. In the author's opinion, these results show Staedler's formulæ to be incorrect, inasmuch as, according to them benzophenone should be obtained on oxidation of the above, and he considers the following formulæ as best in accordance with the known facts, all of which certainly prove that benzile, benzoïn, and benzilic acid do not bear that relation to each other which is commonly assumed, viz., that of anhydride, aldehyde, and acid:—



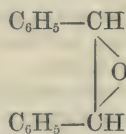
Stilbene.



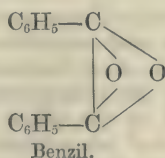
Hydrobenzoïn.



Benzoïn.



Deoxybenzoïn.



The author states that experiments to prepare the compound



$(C_6H_5CO)_2$  either by the action of metals on benzoyl chloride, or by oxidation of dibenzyl  $(C_6H_5CH_2)_2$ , were without result. On heating stilbene with fuming hydrobromic acid to  $150^\circ$ , the former combines directly with one molecule of  $HBr$ .

H. E. A.

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**On some Derivatives of Naphthalene.** By A. FAUST and E. SAAME (Ann. Chem. Pharm. clx, 65—73).

THE following investigation is for the most part a revision of Laurent's well known researches on the chlorine-derivatives of naphthalene. By passing a rapid current of chlorine into fused naphthalene, until the product after cooling has the consistency of butter, and treating it with petroleum naphtha, a crystalline residue of naphthalene tetrachloride is obtained, whilst the filtrate contains monochloronaphthalene and two isomeric dichloronaphthalenes, which can be separated by fractional distillation. On acting again with chlorine on those portions of the distillate which have no constant boiling point, until the mass partially solidifies on cooling, and exhausting with petroleum naphtha, a residue of dichloronaphthalene tetrachloride is obtained, whilst the solution contains heptachlorodinaphthalene. In another experiment the action of chlorine was carried on till the product remained liquid after cooling; on mixing it with petroleum naphtha, crystals of monochloronaphthalene tetrachloride separated after a few days. By the further action of chlorine, enneachlorodinaphthalene is formed, which is the final product.

(1). *Addition-products*.—The following bodies are solids, with hardly any smell; they are sparingly soluble in alcohol, more readily in ether and petroleum naphtha, and very readily in chloroform, from which they crystallise in large colourless, shining, and brittle crystals. On boiling their alcoholic solution with nitric acid and silver nitrate, silver chloride is formed.

*Naphthalene Tetrachloride*,  $C_{10}H_6Cl_4$ .—Large rhombohedrons which melt at  $182^\circ$ , and on boiling with alcoholic potash-solution yield *a*-dichloronaphthalene.

*Monochloronaphthalene Tetrachloride*,  $C_{10}H_7Cl_4$ .—Clinorhombic prisms, melting at  $128^\circ$ — $130^\circ$ . Yields with alcoholic potash, trichloronaphthalene.

*Dichloronaphthalene Tetrachloride*,  $C_{10}H_6Cl_2, Cl_4$ .—Four-sided clinorhombic prisms, melting at  $172^\circ$ , and yielding tetrachloronaphthalene on boiling with alcoholic potash. Boiling nitric acid oxidises it to dichlorothalic acid.

(2). *Substitution-products*.—These compounds are readily soluble in ether, petroleum naphtha, and chloroform, less so in alcohol. They smell like naphthalene, the odour becoming the fainter the more chlorine they contain. Their nitro-compounds are yellow masses, which are difficult to purify, and by the action of sodium carbonate or ammonia are partially converted into a brown colouring matter.

*Monochloronaphthalene*,  $C_{10}H_7Cl$ .—A colourless, strongly refracting oil, which boils at  $250^\circ$ — $252^\circ$ . On dissolving it in fuming nitric acid,

*monochlorodinitronaphthalene*,  $C_{10}H_5(NO_2)_2Cl$ , is formed, soft yellow needles, melting at  $104^\circ$ — $106^\circ$ .

*$\alpha$ -Dichloronaphthalene*,  $C_{10}H_6Cl_2$ .—Prepared from the tetrachloride. Boils at  $280^\circ$ — $282^\circ$ , and solidifies on cooling after some time to a crystalline mass, which melts at  $35^\circ$ — $36^\circ$ .\* By acting on it with bromine, and treating the product with alcoholic potash-solution,  *$\alpha$ -tetrachlorotribromodinaphthalene*,  $C_{20}H_3Cl_4Br_3$ , is formed in long soft white needles, melting at  $74^\circ$ — $76^\circ$ .

*$\beta$ -Dichloronaphthalene*.—Crystallises in brittle shining prisms, melts at  $68^\circ$ , and boils at  $281^\circ$ — $283^\circ$ . It occurs, together with its isomeride, in the fraction boiling at  $280^\circ$ — $285^\circ$ , and crystallises on cooling, whilst the  $\alpha$  compound in the impure state remains liquid and can be removed by pressing the mass between blotting paper.  *$\beta$ -tetrachlorotribromodinaphthalene* was obtained in the same way as the  $\alpha$  compound, and has great resemblance to the latter. It melts at  $71^\circ$ — $73^\circ$ .

*Trichloronaphthalene*,  $C_{10}H_5Cl_3$ .—Crystallises from a mixture of ether and alcohol in brittle prisms, melting at  $81^\circ$ .

*Heptachlorodinaphthalene*,  $C_{20}H_5Cl_7$ .—Crystallises from ether and alcohol in long, yellowish, soft prisms, melting at  $106^\circ$ . On boiling it with alcoholic potash-solution, it becomes colourless, and then crystallises in compact six-sided prisms, which melt at  $100^\circ$ — $102^\circ$ . By fuming nitric acid it is converted into *heptachlorodinitrodinaphthalene*, soft yellowish needles melting at  $104^\circ$ — $106^\circ$ .

*Tetrachloronaphthalene*,  $C_{10}H_4Cl_4$ .—Soft white needles, melting at  $130^\circ$ .

*Enneachlorodinaphthalene*,  $C_{20}H_7Cl_9$ .—Forms, after repeated crystallisation from alcohol, soft white needles, which melt at  $156^\circ$ — $158^\circ$ .

C. S.

### Transformation of Cane-sugar into Glucose by the Action of Light. By E. M. RAULT (Compt. rend. lxxiii, 1049).

EQUAL volumes of a solution of pure cane-sugar, containing 10 grms. of sugar to 50 c.c. of water were introduced into two glass tubes and boiled for several minutes, after which the tubes were hermetically sealed. The two tubes were placed side by side, but whilst one was exposed to the action of light, the other was carefully protected from it. Five months after, May to October, the tubes were examined. Both were found perfectly transparent and free from any microscopic growth. The contents of the tube which had been exposed to the light gave, however, a copious red precipitate with Barreswil's copper test, about one-half of the sugar contained in it having been converted into invert sugar, whereas the contents of the tube which had been kept in the dark gave no precipitate whatever with the copper test. Cane-sugar, when dissolved in water and exposed to the action of light, is, therefore, slowly converted into glucose. A syrup may thus contain a considerable quantity of glucose without having been adulterated.

A. D.

\* Laurent describes a number of modifications of this compound, but the authors could not find any other form than that described above.

**Transformation of Glucose into Monatomic and Hexatomic Alcohols.** By G. BOUCHARDAT (Compt. rend., lxxiii, 1008—1011).

IN a preceding communication the author found that by the action of sodium-amalgam on inverted milk-sugar, dulcite is formed; by a more attentive study of the reaction, monatomic alcohols such as ethylic, isopropylic, and hexylic alcohols are found to be produced. The author has experimented on glucose, milk-sugar and inverted milk-sugar.

A concentrated solution of glucose is treated with sodium amalgam containing 3 per cent. sodium, the evolved gas being allowed to pass into water. The alkaline liquid is neutralised with sulphuric acid, and on distillation and treatment with potassic carbonate, yields an oily layer consisting of ethylic, isopropylic and hexylic alcohols, the two former being separated by conversion into the iodides. The liquid which remains behind in the retort yields, after separation of the sodic sulphate, a large quantity of mannite.

Milk-sugar under the same circumstances gives ethylic, isopropylic and hexylic alcohols, the residue containing dulcite.

Inverted milk-sugar yields, instead of dulcite alone, a mixture of dulcite and mannite.

A. P.

**On the Acetyl-derivatives of Carbo-hydrates, Mannite and its Isomerides, and certain other Vegetable-products.** By P. SCHÜTZENBERGER (Ann. Ch. Pharm. clx, 74—100, from Ann. Chim. Phys. [4], xxi, 235).

IN a notice published in 1865 (Compt. rend., lxi, 485), the author stated that acetic anhydride acts with great facility on a large number of organic compounds having the character of polyatomic alcohols, converting them in a short time into acetylated derivatives, the degree of substitution in which depends upon the proportion of the anhydride employed, the temperature, and the duration of the action. The present paper contains a detailed description of these compounds.

Acetic anhydride is preferable to acetyl chloride for the reactions under consideration, because by its use the presence of hydrogen chloride is avoided (this substance frequently causing other changes to ensue): frequently, too, the reaction takes place in open vessels, or at least under a small pressure at temperatures between  $130^{\circ}$  and  $160^{\circ}$ .

(1.) *Cellulose and Acetic Anhydride*.—Carded cotton-wool or Swedish filter-paper heated for two hours to  $180^{\circ}$  with six or eight times its weight of the anhydride, is perfectly dissolved, forming a thick dark brown syrup, from which water precipitates thick dirty flocks much resembling coagulated albumin; this precipitate well washed and dried is soluble in glacial acetic acid, forming a coloured liquid which is rendered perfectly clear and colourless by treatment with purified animal charcoal: water precipitates from this solution white flakes which, after drying, have the composition of *tri-acetyl-cellulose*  $\left. \begin{matrix} \text{C}_6\text{H}_7\text{O}_2 \\ (\text{C}_2\text{H}_3\text{O})_3 \end{matrix} \right\} \text{O}_3$ .

This body forms a white powder insoluble in water, alcohol, ether, and benzene: soluble in glacial acetic acid and in sulphuric acid, from which solutions it is precipitated unchanged by water. On saponifica-



tion, *i.e.*, when boiled with a standard solution of caustic soda, it regenerates cellulose and three equivalents of sodium acetate. This method of determining the amount of acetyl present was employed for all the compounds investigated.

From the formation of triacetyl-cellulose (as well as that of trinitro-cellulose by the action of nitric acid), it appears that cellulose is a triatomic alcohol  $\left. \begin{matrix} \text{C}_6\text{H}_7\text{O}_2 \\ \text{H}_3 \end{matrix} \right\} \text{O}_3$ .

When smaller proportions of anhydride, and a temperature lower than  $150^\circ$  are employed, cotton-wool only swells up without dissolving, giving apparently mono- and di-acetyl-cellulose, which are insoluble in all media save sulphuric acid, and cannot be separated from unaltered cotton-wool.

(2.) *Starch and Acetic Anhydride*.—The products of this action vary with the state of aggregation of the starch, and with the purity of the anhydride used. When anhydride containing 10 to 15 per cent. of acid acts at  $140^\circ$  on one-third or somewhat more of starch-powder, this latter swells up without dissolving, at any rate in more than a minute proportion: after washing with water, a white powder is obtained, insoluble in water, alcohol, ether, and glacial acetic acid, and not yielding a blue colour with iodine. Saponification reproduces the original insoluble starch rendered blue by iodine: dried at  $120^\circ$ , this powder has the composition of triacetyl-amidin  $\left. \begin{matrix} \text{C}_6\text{H}_7\text{O}_2 \\ (\text{C}_2\text{H}_3\text{O})_3 \end{matrix} \right\} \text{O}_3$ . If the mixture of starch and anhydride be heated to  $150^\circ$ , however, the swollen mass dissolves, forming an amber-coloured syrup, from which water precipitates white flocks insoluble in water, alcohol, and ether, but soluble in glacial acetic acid. This product, when purified in the same manner as triacetyl-cellulose, forms a white powder easily saponifiable by dilute soda-solutions, with formation of soluble starch, precipitable by alcohol from the aqueous solution obtained, and rendered blue by iodine; on analysis, this white powder gives numbers identical with those obtained with the former compound; it is powerfully dextrorotatory, giving the value  $[\alpha] = 120.8$ . As Béchamp finds that pure soluble starch gives the value  $[\alpha] = 216$ , and the triacetyl derivative contains in 100 parts 55 of active substance, the calculated value for  $[\alpha]$  is  $118.8^\circ$ . At temperatures higher than  $150^\circ$ , a similar triacetyl body is obtained, yielding on saponification only dextrin. No substances containing more than three atoms of acetyl have been obtained.

(3.) *Glycogen and Acetic Anhydride*.—Liver-glycogen heated to  $155^\circ$  with excess of anhydride, swells up without dissolving; the product well washed with water has the composition of triacetyl-glycogen  $\left. \begin{matrix} \text{C}_6\text{H}_7\text{O}_2 \\ (\text{C}_2\text{H}_3\text{O})_3 \end{matrix} \right\} \text{O}_3$ , and is insoluble in cold or hot water, alcohol, ether, and acetic acid; saponification reproduces either glycogen or an analogous body, which is dextro-rotatory, giving the value  $[\alpha] = +56^\circ$ .

(4.) *Gum Arabic and Acetic Anhydride*.—Pure powdered arabin and twice its weight of anhydride heated to  $150^\circ$ , form an insoluble substance which, after treatment with boiling water, and washing with

alcohol, has the composition of *diacetyl-arabin*  $C_6H_5(C_2H_3O)_2O_5$ : the formula, however, should be doubled, inasmuch as the saturated acetyl derivative (obtained by heating to  $180^\circ$  for 5—6 hours with 6—8 parts of anhydride) has the composition  $C_{12}H_{15}(C_2H_3O)_5O_{10}$ : both these products are white amorphous powders.

(5.) *Inulin and Acetic Anhydride*.—The inulin from *Georgina purpurea* (dahlia-inulin) is not identical with that from *Inula Helenium* (elecampane-inulin); their respective rotatory powers are—

Dahlia-inulin	$[\alpha] = -26^\circ$
Elecampane-inulin	$[\alpha] = -32^\circ$

(a.) On heating to boiling for  $\frac{1}{4}$  hour either of these varieties of inulin with its own weight of anhydride and twice as much glacial acid, products of the same constitution are obtained in either case, giving numbers agreeing with the formula  $C_{12}H_{17}(C_2H_3O)_3O_{10}$ , the sole difference between them being in their rotatory powers, which are—

Triacetyl-dahlia-inulin	$[\alpha] = -20^\circ$
Triacetyl-elecampane-inulin	$[\alpha] = -32^\circ$

These substances are soluble in water, acetic acid, and alcohol; insoluble in ether.

(b.) On heating to boiling 1 part of either variety of inulin and 2 parts of anhydride for a quarter of an hour in a long-necked flask, products are formed which differ from the preceding in not being precipitable by ether from the acid liquid obtained: they are insoluble in water, but soluble in alcohol or dilute acetic acid; purified by animal charcoal in alcoholic solution, and dried at  $100^\circ$ , the elecampane-inulin derivative gives numbers indicating a *pentacetyl compound*  $C_{12}H_{15}(C_2H_3O)_5O_{10}$ , while the dahlia-inulin derivative is a *tetra-acetyl product*,  $C_{12}H_{16}(C_2H_3O)_4O_{10}$ : their respective rotatory powers are—

Pentacetyl elecampane-inulin	$[\alpha] = -25^\circ$ (mean)
Tetracetyl dahlia-inulin	$[\alpha] = -14^\circ$

(c.) Either variety of inulin heated to boiling for half an hour with 3 parts of anhydride, gives a product precipitable on adding water, the precipitate being soluble in alcohol and insoluble in water. The elecampane-inulin derivative has the composition  $C_{12}H_{13}(C_2H_3O)_7O_{10}$  and has a feeble dextrorotatory action; whilst that from dahlia-inulin is  $C_{12}H_{14}(C_2H_3O)_6O_{10}$ . In another experiment under almost the same conditions, the end-product from elecampane-inulin gave numbers agreeing with those required for an octacetyl derivative; from which it is inferred that, instead of having the formula  $C_6H_{10}O_5$  (as formerly supposed for inulin), elecampane-inulin is  $C_{12}H_{22}O_{11}$ , while dahlia-inulin is  $C_{12}H_{20}O_{10}$ .

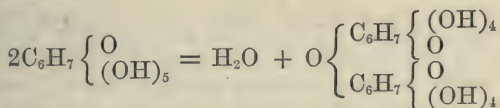
(d.) Dahlia-inulin heated to  $160^\circ$  in a sealed tube with 2—3 parts of anhydride is partly dehydrated, and forms two acetyl derivatives: one is soluble in water, and has the rotatory power  $[\alpha] = +55^\circ$ , the other is insoluble in water, and has the value  $[\alpha] = +35.5$ ; both, however, give numbers agreeing with a tetracetyl derivative. Saponified with soda, the soluble body gives a resinous mass  $C_{12}H_{16}O_8$ , or inulin minus  $2H_2O$ .

Elecampane-inulin under the same conditions gave only a black humous mass, together with a trace of dextro-rotatory syrup.

In estimating the acetyl contained in the foregoing inulin derivatives the decomposition was effected with normal sulphuric acid: caustic soda gives rise to other acid products besides acetic acid, and hence always gives too high numbers: the same applies to the sugar derivatives hereafter described.

(6.) *Glucose and Acetic Anhydride*.—Pure crystallised glucose dried at  $100^{\circ}$  is easily attacked at  $120^{\circ}$  by acetic anhydride, the resulting products differing with the proportion of acid admixed with the anhydride. One part of glucose and  $2\frac{1}{2}$  of anhydride heated in an open vessel react readily, the action being over in a few moments; a little water being added to destroy the anhydride, and the whole evaporated to dryness on the water-bath, an amorphous residue soluble in water, and of a very bitter taste, is obtained. Boiling benzene only partly dissolves this residue, the soluble part being *triacetyl-glucose*,  $C_6H_9(C_2H_3O)_3O_6$ . This body heated to  $140^{\circ}$  by itself or with acetic anhydride, loses water, giving *triacetyl-glucosan*  $C_6H_7(C_2H_3O)_3O_5$ , insoluble in water, soluble in dilute acetic acid. The insoluble part dissolved in water, and decolorised by animal charcoal, yields on evaporation *in vacuo* an amorphous light yellow bitter mass, very soluble in water, and soluble in alcohol: this is *diacetyl-glucose*,  $C_6H_{10}(C_2H_3O)_2O_6$ .

Glucose heated with a large excess of anhydride to  $160^{\circ}$  for 6 hours, does not form a glucose derivative as was expected, but one derived from two molecules of glucose, which coalesce, with loss of  $H_2O$ , according to the equation—



All the eight hydrogen-atoms of the hydroxyl present in this *diglucose* are replaced by acetyl, forming  $C_{12}H_{14}O_3 \left\{ \begin{array}{c} (C_2H_3O)_8 \end{array} \right\} O_8$ , which is either identical or isomeric with the compounds of the same composition obtained by the action of acetic anhydride on cane- and milk-sugars; in water it is insoluble, in alcohol soluble; it has no marked taste of any kind.

All the acetylated derivatives of glucose are dextrorotatory.

(7.) *Cane-sugar and Acetic Anhydride*.—Cane-sugar heated with  $\frac{1}{2}$  pt. acetic anhydride, and 3—4 parts glacial acid entirely dissolves: ether throws down a yellow tarry precipitate, which, when dried *in vacuo* over quick lime, and finally at  $100^{\circ}$ , is a solid substance soluble in water and alcohol, of a weak sweet taste, somewhat inclined to bitter, insoluble in ether and benzene; this is *monoacetyl-saccharose*  $C_{12}H_{21}(C_2H_3O)O_{11}$ . The ethereal filtrate from this substance evaporated to dryness, dissolved in water, and decolorised by animal charcoal, gives numbers intermediate between those required for *tetra-* and *penta-acetyl-saccharose*: this is probably a mixture of these two bodies; it is soluble in water, alcohol, and ether.

Heated with a large excess of anhydride, cane-sugar yields *hepta-* and



*octo-acetyl saccharose*,  $C_{12}H_{15}(C_2H_3O)_7O_{11}$  and  $C_{12}H_{14}(C_2H_3O)_8O_{11}$ , as gummy amorphous bodies insoluble in water, and much resembling the octo-acetyl diglucose obtained with glucose.

(8.) *Milk-sugar and Acetic Anhydride*.—Milk-sugar is less easily acted on than cane-sugar; after long boiling in an open vessel, perfect solution ensues. From the product water precipitates *octacetyl milk-sugar*,  $C_{12}H_{14}(C_2H_3O)_8O_{11}$ ; the solution contains *tetracetyl milk-sugar*, which forms indistinctly shaped crystals of a bitter taste: these bodies have the rotatory powers  $[\alpha] = +31^\circ$ , and  $[\alpha] = +50.1^\circ$  respectively.

(9.) *Mannite and Acetic Anhydride*.—Mannite heated in an open vessel with anhydride containing 10–15 per cent. of acid dissolves; on cooling, the product becomes a mass of indistinctly shaped crystals, which, after separation of syrupy mother-liquor by filtration through asbestos by means of a pumping arrangement, and washing with alcohol, forms a solid, white, very light substance, apparently homogeneous, scarcely soluble in boiling alcohol, soluble in water and acetic acid, insoluble in ether: it has a weak, sweet and bitter taste, and is feebly dextrorotatory; its composition is that of a monoacetyl derivative of a di-mannitic anhydride,  $C_{12}H_{24}O_{10}$ , viz.,  $C_{12}H_{23}(C_2H_3O)O_{10}$ . On saponification, this body yields a faintly sweet substance apparently identical with Berthelot's mannitan, whence it appears that this latter body has the formula  $C_{12}H_{24}O_{10}$ .

By the further action of the anhydride, a thick syrup is obtained which, on treatment with water, gives a crystalline precipitate, crystallisable from boiling water or alcohol; this is *hexacetyl mannite*  $C_6H_8(C_2H_3O)_6O_6$ ; it melts at  $100^\circ$ , and becomes crystalline on cooling. It has no action on polarised light. The syrupy mother-liquors of this compound give on evaporation an extremely bitter substance easily soluble in water, acetic acid, and alcohol; it is dextrorotatory:  $[\alpha] = 22.6^\circ$ , which is remarkable, as mannite has no rotatory power. It has the composition  $C_6H_{10}(C_2H_3O)_2O_5$ ,\* and appears to be identical with the acetylated mannite which Berthelot obtained by the action of glacial acetic acid.

(10.) *Synthesis of Glucosides by means of the Acetyl Derivatives of the Sugars*.—Attempts to synthesize salicin from sodium-saligenin and acetyl-glucose, met with only partial success; when these two substances are heated together in presence of benzene or alcohol, there is produced a small quantity of a substance which forms glucose and saliretin on boiling with diluted sulphuric acid; this is obtained pure by evaporation to dryness, solution in water, precipitation by lead acetate, and decomposition by sulphuretted hydrogen; and finally, by evaporation to dryness in vacuo, there is obtained an amorphous yellowish brittle mass, soluble in water and alcohol. The majority of the substances employed, however, react differently, *aceto-saliretin*  $C_{14}H_{11}(C_2H_3O)O_2$  (?), and *sodium glucinate* being formed: the former, which yields saliretin and sodium acetate on saponification, is likewise obtainable by the action of acetic anhydride on saliretin.

Diaceto-saccharose and sodium-saligenin, heated in an open vessel,

\* In the original paper in the *Annales de Chimie et de Physique*, the constitution  $C_6H_8(C_2H_3O)_5O_4$  is erroneously attributed to this body; the analytical numbers agree with that given above.

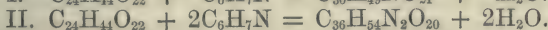
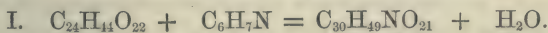
together with absolute alcohol, also form a small quantity of a glucoside which splits into glucose and saliretin; the greater portion of the substances, however, is converted into aceto-saliretin and the sodium salt of an acid very similar to glucinic, which may be termed *saccharinic acid*. The sodium salt,  $C_{12}H_{19}NaO_{10}$ , separates in small white crystals from boiling absolute alcohol; it is very soluble in water, gives with basic lead acetate a precipitate soluble in excess of the acetate, and yielding the acid itself by decomposition with sulphuretted hydrogen; the acid forms a very sour syrup.

The lead precipitate obtained by treating saligenin with lead acetate also yields, when heated with an aqueous solution of acetyl-glucose or -saccharose, a considerable quantity of a glucoside which splits into saliretin and glucose on treatment with acids; it is, however, uncrystallisable.

Rhamnetin (obtained by boiling rhamnegin, its glucoside, with dilute sulphuric acid) dissolved in caustic potash to saturation gives a precipitate with lead acetate; this precipitate heated in sealed tubes to  $140^{\circ}$  with solution of diacetyl-saccharose, gives a colourless liquid containing glucose, and a yellow insoluble portion which is a mixture of rhamnetin and the lead compound of its glucoside; this portion treated with sulphuretted hydrogen, after thorough washing, yields a dark yellow liquid, from which an easily soluble amorphous dark yellow dye-stuff is obtainable by evaporation; this is extremely like rhamnegin in its properties, dyes the same tints, and splits on boiling with acids into glucose and rhamnetin, which is insoluble in water. C. R. A. W.

### Nitrogenous Compounds from Milk-sugar. By ROBERT SACHSSE (Deut. Chem. Ges. Ber., iv, 834).

By the action of aniline on milk-sugar, the author has obtained two bodies, whose formation is expressed by the equations—



Attention may be called to the resemblance of these reactions to those realised by Hugo Schiff with aniline and the aldehydes. The precise conditions under which the one or the other, or a mixture of the two may be obtained, have not been ascertained.

*Preparation.*—On heating one part of sugar with two parts of aniline, in an open flask, the former dissolves with much frothing, but without evolution of gas; about an equal volume of alcohol is then added, and the liquid filtered, when, after standing some time, the filtrate almost solidifies to a mass of crystals. These are washed first with alcohol, then with ether, and finally dissolved in hot water; 5—6 vols. of absolute alcohol are added, and a large quantity of ether. Brilliant white crystalline needles then separate out after some time, which may be dried at  $100^{\circ}$ . Both bodies are very soluble in water, difficultly in absolute alcohol, almost insoluble in ether; they reduce alkaline copper solutions. Grape-sugar, mannite, and other carbohydrates also dissolve readily in aniline.

H. E. A.



**On the Behaviour of Starch and Dextrin to Iodine and Tannic Acid.** By V. GRIESSMAYER (*Ann. Ch. Pharm.* clx, 40—56).

THE author describes minutely the effects produced on the addition of a weak iodine solution, and of tannic acid solution, to starch solutions which have been kept for various lengths of time exposed to the air at the ordinary temperature, the conclusion at which he arrives being that filtered starch-paste is in a state of continual chemical change. The solutions employed were:—1. A decimille-normal iodine solution. 2. An aqueous solution of tannic acid containing 3·5 grm. pure tannin in 300 c.c.—3. A filtered starch-solution, which was always prepared by triturating 3·5 grm. wheaten starch with 50 c.c. cold water, pouring into 300 c.c. boiling water, boiling for a few minutes, and then filtering whilst hot. On adding either of the reagents to 20 c.c. starch solution, the following reactions were observed:—

*1st day.*—With iodine, 1 to 7 c.c. produced no coloration whatever; 7·5 to 8 c.c., a violet shade; 9—10 c.c., a faint blue, which became distinctly blue only after 16 c.c. had been added. With tannic acid, the first drop produced a precipitate of tannate of starch, which redissolved on shaking; the second drop a permanent precipitate. This latter is dissolved on warming, but reappears on cooling. No alteration in these reactions on the second and third days.

*4th day.*—A flocculent separation was visible in the starch-solution, which, after filtration, exhibited the same reactions as on the first day.

*5th day.*—11 c.c. iodine gave a faint violet; with 17 c.c., a blue tinge, becoming more and more intense, up to 25 c.c., but more of a lilac colour. Tannic acid: same reaction as on first day.

*6th day.*—With iodine, a perceptible violet shade only after 20 c.c., but slightly deepened up to 25 c.c. A few drops of tannic acid caused a precipitate, which disappeared however on shaking; a permanent precipitate only after several drops.

*7th day.*—22 c.c. iodine gave a violet tint, changing to red with 25 c.c., and becoming pure red with 30 c.c., 10 c.c. of tannic acid were required to cause opalescence, a slight precipitate separating after some time.

*8th day.*—A red tinge with 10 c.c. iodine, becoming gradually more distinct, until perfectly red with 20 c.c. An excess of tannic acid causes opalescence.

*9th day.*—A red coloration with iodine; no precipitate with tannic acid.

*10th day.*—No coloration with iodine; a yellowish tinge with an excess. Also no reaction with tannic acid. The solution then remains one to two days in this state, after which sugar is formed, and may be easily detected by Fehling's solution. After another week the sugar has disappeared, and the liquid is strongly acid. The author notes that decinormal iodine solution is perfectly decolorised by exposure to the air for about six weeks; a millinormal solution in three to six days, and a decimillinormal solution on standing over night. This is due, not to the evaporation of iodine only, but in great measure to the formation of hydriodic acid.

The author's interpretation of the above results is, that the solution



obtained by treating starch with hot water passes through three stages of change when allowed to stand, until it is finally converted into glucose and other products. It is impossible to obtain a starch solution quite free from dextrin in the above manner, for perfectly fresh solution was never coloured blue by the addition of 6—10 c.c. decimillenormal iodine-solution but always violet, the red colour of the iodised dextrin forming violet with the blue iodised starch; the first drop of tannic acid also gave a precipitate, which disappeared on shaking, because of the greater affinity of the tannic acid to dextrin than to starch, in consequence of which it does not combine with the latter till the whole of the dextrin is neutralised.

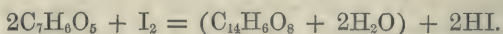
A starch-solution allowed to stand about a week, during which time a flocculent precipitate is deposited, yields a red-colour with 10—20 c.c. of decimillenormal iodine-solution, which colour corresponds to a dextrin obtained both by mashing and in the artificial preparation of dextrin. It is nearly always accompanied by a second dextrin, which forms a *colourless* compound with iodine. Dextrin I may moreover be readily detected in the presence of much starch by operating with dilute iodine; no starch reaction is observed until the whole of the dextrin is saturated. With starch in the presence of much dextrin, no starch reaction is obtained, until a concentrated iodine-solution is employed, so that both bodies may be readily detected when in the same solution.

Tannic acid does not precipitate dextrin, and when starch is also present, the precipitate redissolves until the whole of the dextrin is fixed.

If the starch-solution is allowed to stand more than a week in contact with air at a certain stage, the addition of decinormal iodine drop by drop, causes a red streak, which, however, immediately disappears; the next day even this is perhaps not observed, and yet sugar is not to be detected in the solution, and in this case the addition of an excess of iodine causes no coloration; in the first the reaction of dextrin I is obtained. The body now present in the liquid the author terms dextrin II, *dextrin passive to iodine*, for which it has a greater affinity than dextrin I. He considers that it is also co-existent with dextrin I in the fresh starch solution, since 5—6 c.c. of the weak iodine may be added without causing the slightest coloration.

*Tannic Acid in its action on Iodine, Starch, and Iodised Starch.*—By the addition of an excess of tannic acid to an iodine-solution, the latter becomes gradually decolorised. Tannic acid also causes the decoloration of iodised starch-solution. In both cases the iodine is reduced to hydriodic acid. In order to investigate the action of iodine on tannic acid, 60 grms. iodine, 60 grms. tannic acid, and about 800 c.c. water were digested in a stoppered flask on the water-bath, at a mean temperature of about 92°, the flask being repeatedly shaken. After some days the whole had dissolved to a dark brown liquid, from which over night a voluminous precipitate of gallic acid separated, but was redissolved on heating. After 4—6 days a permanent dark black crystalline precipitate formed on the sides and bottom of the flask, to obtain a good yield of which, the operation had to be continued for 6—8 weeks. The black substance was purified by digestion with dilute ammonia, and washing with water; a yellow body was thus obtained, which was dis-

solved in soda, re-precipitated by acid, and then washed until free from sodium chloride. The composition and reaction of this product proved it to be ellagic acid,  $C_{14}H_6O_8 + 2 \text{ aq.}$ , the yield being about one-fourth of the tannic acid employed. The filtrate from the crystals, which deposited much gallic acid on standing in the flask, was evaporated to a small bulk, and the remaining liquid decanted from the gallic acid which had separated. In order to prove the presence of sugar and hydriodic acid, which it was probable were also products of the reaction, an excess of a stiff starch-paste was added to a portion, to remove free iodine, and the whole allowed to stand an hour or two, the supernatant liquid being then removed by a syphon. The addition of a crystal of potassium nitrite to this liquid at once produced a deep blue coloration, proving the presence of hydriodic acid. In testing for sugar, the iodine, hydriodic acid and gallic acid were removed by basic lead acetate, the filtrate saturated with hydrogen sulphide, evaporated somewhat, and finally Fehling's solution added, when, on warming, cuprous oxide was deposited. The products of the action of iodine on tannic acid are therefore ellagic, gallic, and hydriodic acids and sugar. Doubtless the tannin is first split up into gallic acid and sugar, the gallic acid afterwards yielding ellagic acid, in proof of which the following experiment was made. 10 grms. gallic acid, 10 grms. iodine, and 160 c.c. water were digested together for several days on the water-bath; the same characteristic black crystals as above were obtained, and proved to be ellagic acid; after adding an excess of basic lead acetate to the filtrate, &c., no sugar could be detected. The reaction is probably



H. E. A.

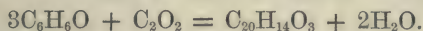
**On Aurine.** By R. S. DALE and C. SCHORLEMMER (Proc. Lit. Phil. Soc., vol. xi, No. 2).

A SHORT note on this subject has already appeared in the number of this Journal for July, 1871 (p. 446).

To obtain the pure colouring matter from the commercial product, the latter is dissolved in alcohol and treated with ammonia. A crystalline precipitate, a compound of aurine with ammonia, separates out, whilst the other bodies present remain in solution. The ammonia-compound, after being washed with alcohol by means of Bunsen's filter pump, is decomposed by dilute acetic acid and further purified by repeated crystallisation from strong acetic acid. The specimens thus obtained retain most obstinately varying quantities of water and acetic acid; a fact which has also been observed by Fresenius, who has lately published a note on the same subject.\* From concentrated hydrochloric acid, aurine crystallises in fine hair-like, red needles, which when dried at  $110^\circ$ , contain a large quantity of hydrochloric acid. To obtain pure aurine, a dilute alkaline solution was precipitated with dilute hydrochloric acid, and the precipitate washed by the filter-pump, but this product also contains hydrochloric acid, which is only given off above  $110^\circ$ . By spontaneous evaporation of an alcoholic solution,

\* J. pr. Chem., No. x, 1871.

aurine is obtained in dull red crystals with a green metallic lustre. Dried at  $110^{\circ}$  they contain no alcohol, but still 5.4 per cent. of water, which escapes only between  $140^{\circ}$ — $180^{\circ}$ , the crystals not changing their appearance at all; they may also be heated to  $200^{\circ}$  without any further alteration, which fact does not agree with Fresenius's observation, that aurine crystallised from alcohol or acetic acid melts at  $150^{\circ}$ . Aurine, dried at  $200^{\circ}$ , appears to have the composition  $C_{20}H_{14}O_3$ ; if this formula is correct, its mode of formation may be expressed by the equation—



The compound dried at  $110^{\circ}$ , is  $C_{20}H_{14}O_3 + H_2O$ . Caro and Wanklyn obtained, by the action of nitrous acid upon rosaniline, a body which they believe to be identical with aurine, and to which they give the formula  $C_{20}H_{16}O_3$ ,\* differing from that above given only by two atoms of hydrogen.

Nascent hydrogen converts aurine into *leuco-aurine*,  $C_{20}H_{18}O_3$ ; this reduction is best effected by acting with zinc-dust on a solution of aurine in acetic acid; it is thus obtained quite colourless. whilst by reducing it in an alkaline solution at the same time, a dark resinous body is formed, from which the leuco-aurine cannot be easily freed.

By passing sulphur dioxide into a hot alcoholic solution of aurine, brick-red crystals are separated, a compound of aurine with sulphur dioxide, which undergo no change when exposed to the air, and are decomposed only above  $100^{\circ}$ , when they split up into aurine and sulphur dioxide. With the bisulphites of the alkali-metals, aurine forms colourless compounds, which are soluble in water and alcohol, and can be obtained in fine crystals. They are decomposed by acids as well as by alkalis.

By heating aurine with alcoholic ammonia to  $140^{\circ}$ ,† the so-called *red coralline* is obtained, a body resembling aurine, but dyeing a redder shade. This body has also been obtained in fine crystals.

C. S.

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**On some Derivatives of Phthalic Acid.** By A. FAUST (Ann. Chem. Pharm. clx, 57—65).

**NITROPHthalic acid**,  $C_6H_3NO_2(CO_2H)_2$ , is obtained by digesting phthalic acid with a mixture of equal parts of sulphuric and nitric acid, and diluting with water after 24 hours. It crystallises from ether in pale yellow prisms, which melt at  $208^{\circ}$ — $210^{\circ}$ , the anhydride being formed. This acid appears to be identical with that which Laurent obtained by boiling naphthalene with nitric acid.  $C_6H_3(NO_2)_4O_4K_2$ , crystallises from hot alcohol without water of crystallisation; by precipitating its aqueous solution with alcohol, yellow needles containing one molecule of water are obtained.  $C_6H_4(NO_2)_4O_4K$  is precipitated in form of white needles by mixing a concentrated solution of the acid and the neutral potassium salt.  $C_6H_3(NO_2)_4O_4(NH_4)_2$  is obtained in large orthorhombic prisms by dissolving the acid in strong aqueous ammonia and adding

\* Proc. Roy. Soc., xv, 210.

† The original paper gives  $110^{\circ}$  by misprint.—C. S.



absolute alcohol.  $C_8H_4(NO_2)_4NH_4 + 2H_2O$  forms fine yellowish-white needles, which are obtained by mixing the acid with an alcoholic solution of the neutral salt.  $C_8H_3(NO_2)_4Ba + H_2O$  crystallises from the supersaturated aqueous solution in yellowish shining laminae, sparingly soluble in water.  $C_8H_3(NO_2)_4Zn + 1\frac{1}{2}H_2O$  is a yellow crystalline powder, formed by boiling the aqueous solution of the acid with zinc oxide.  $C_8H_3(NO_2)_4Pb + 1\frac{1}{2}H_2O$  and  $C_8H_3(NO_2)_4Ag_2$  are white precipitates, sparingly soluble in water. The ethylic ether,  $C_8H_3(NO_2)_4(C_2H_5)_2$ , is easily formed by passing hydrochloric acid gas into an alcoholic solution of the acid and applying heat from time to time. It is a yellowish, scentless oil, boiling above  $300^\circ$  with decomposition. The acid ether,  $C_8H_4(NO_2)_4C_2H_5$ , is formed by the same reaction in the cold. It is a crystalline solid and a strong monobasic acid.

By reducing nitrophthalic acid with tin and hydrochloric acid, no amidophthalic acid is formed, but only a amidobenzoic acid.

*Bromophthalic acid*,  $C_6H_3Br(CO_2H)$ . By acting with an excess of bromine upon phthalic acid at  $180^\circ$ — $200^\circ$ , a large quantity of the acid is left unaltered, which can be separated from the brominated acid formed by crystallisation, the latter remaining in the mother-liquors from which the potassium salt was prepared. After purifying this salt by repeated crystallisation from alcohol, it was decomposed by sulphuric acid and the solution shaken with ether and evaporated. Bromophthalic acid is a white powder, readily soluble in ether, alcohol, and water.

$C_8H_3BrO_4K_2 + 2H_2O$  forms large shining deliquescent needles.  $C_8H_3BrO_4Ba + 2H_2O$  is a white, crystalline powder, sparingly soluble in water.  $C_8H_3BrO_4Pb$  is almost insoluble in water, but soluble in boiling dilute acetic acid, from which it separates as a crystalline powder.  $C_8H_3BrO_4Cu$  is a pale-blue, and  $C_8H_3BrO_4Ag_2$  a white, curdy precipitate. The ethylic ether is obtained in a similar way as that of the nitro-acid, and forms a pale-yellow oil.

*Dichlorophthalic acid*,  $C_6H_2Cl_2(CO_2H)_2$ , is readily formed by boiling dichloronaphthalene tetrachloride with common nitric acid. It is soluble in ether, alcohol, and water, and crystallises from the hot aqueous solution slowly in yellowish, compact prisms. It melts at  $183^\circ$ — $185^\circ$  and by repeated sublimation is converted into the anhydride, which resembles benzoic acid, and melts at  $187^\circ$ .

$C_8H_2Cl_2O_4Ba + H_2O$  separates in prisms on mixing an ammoniacal solution of the acid with barium chloride.  $C_8H_2Cl_2O_4Ca + 4H_2O$  forms yellowish prisms on mixing the ammoniacal solution of the acid with calcium chloride.

C. S.

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**On Dibromobenzene-sulphonic Acid.** By A. WOELZ (Zeitschr. f. Chem. [2], vii, 353).

THIS compound and some of its salts have already been described by R. Douglas Williams (Zeitschr. [2], vi, 302). The author had at the same time prepared this acid in order to obtain from it a triad phenol and one of the tricarbon acids of benzene, and he finds that his acid contains 3 mol. of water, whilst that of Williams contains only two.

The following salts were prepared:— $(C_6H_3Br_2SO_3)_2Ba$ , fine soft pearly laminae, sparingly soluble in cold, readily in hot water.  $C_6H_3Br_2SO_3K$ , shiny fascicular needles.  $(C_6H_3Br_2SO_3)Ca$ , silky fascicular needles.  $(C_6H_3Br_2SO_3)_2Pb + 3H_2O$ , rhombic scales, readily soluble in water.  $(C_6H_3Br_2SO_3)_2Cu$ , long shining laminae, containing apparently 14 mol. of water.  $C_6H_3Br_2SO_3NH_4$  crystallises in shining needles from a concentrated solution, and forms, on slow evaporation, compact plates. The author believes that his acid is isomeric with that of Williams, and that described some years ago by Schmitt.

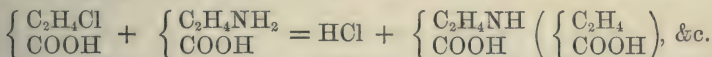
By fusing the potassium salt with caustic potash, only a small quantity of a brown silky substance was obtained, from which no definite compound could be isolated.

In order to obtain a tribasic acid, an intimate mixture of the potassium salt and potassium cyanide was heated in a current of carbonic acid; a small quantity of an oily product was formed, which, when treated with an alcoholic potash-solution, evolved ammonia. From the alkaline solution an acid was obtained, the quantity of which was too small for further investigation, although to prepare it a large quantity of dibrombenzene had been used.

C. S.

**Note on Diethylidenelactamic Acid.** By W. HEINTZ (Ann. Ch. Pharm. clx, 35—39).

THE author has been almost accidentally led to the discovery of this acid, which he was unable to find amongst the products of the action of ammonia on *a*-chloropropionic acid. As there was a possibility of the formation of both di- and triethylidenelactamic acids by the action of *a*-chloropropionic acid on alanine—



he was led to prepare a quantity of alanine, in doing which, Strecker's method was followed, with the one exception that the mistake was made of first adding the hydrochloric and then the hydrocyanic acid to the aldehyde-ammonia.

It is not certain, although probable, that this circumstance influenced the formation of the acid in question. After separation of the chlorine by plumbic hydrate, and of the excess of lead by hydrogen sulphide, and evaporation, no crystals of alanine were obtained; a small quantity only crystallised out on the addition of alcohol, and a further small quantity after evaporation, addition of ammonia, and then of alcohol. The alcoholic filtrate was evaporated, boiled with baric hydrate to expel the ammonia; the barium exactly precipitated with sulphuric acid; and the filtrate digested with cupric oxide. On evaporation, blue indistinctly crystalline grains were deposited, which were purified by washing first with weak, then with strong alcohol, and recrystallisation. From this copper salt diethylidenelactamic acid was readily obtained by decomposing with hydrogen sulphide, the acid

separating from the concentrated aqueous solution in very fine microscopic needles, easily soluble in water, although much less so than diethylenelactamidic acid, and also less soluble than alamine. The copper salt is not very soluble in water, and almost insoluble in alcohol. The crystals are a lighter blue than the alanine copper salt; their composition is  $C_6H_9CuNO_4 + 3aq$ .

H. E. A.

**Frangulic Acid a Derivative of Anthracene.** By AUG. FAUST  
(Zeitschr. f. Chem. [2] vii, 340).

IN a previous communication\* on the colouring matter of the bark of the berry-bearing alder (*Rhamnus frangula*), the author stated this compound to be a glucoside—to which the name of Frangulin was given—which, by the action of alkalis or acids, was split up into sugar and frangulic acid, the latter having, according to his analysis, the composition  $C_{14}H_{10}O_5 + aq$ .

He now finds that on heating this acid with zinc-dust, anthracene is obtained, a proof that it is an anthracene derivative.

H. E. A.

**On the Origin and Properties of Monochlorocitraconic Acid.**  
By J. GOTTLIEB (Ann. Ch. Pharm., clx, 101—117).

CRYSTALLISED citraconic acid dissolved in strong hydrochloric acid and heated to  $100^\circ$  yields, by the cautious addition of potassium chlorate in small portions at a time, an acid which is obtainable as a yellowish, clear, syrupy liquid by evaporation to dryness, exhausting the residue with ether, and distilling off the ether from the extract thus obtained. On heating, this acid gives a copious sublimate of monochlorocitraconic acid and a brown sticky residue.

The same acid is obtained by treatment with aqua regia, or by the action of gaseous chlorine on an aqueous solution of citraconic acid. By precipitating the dilute aqueous solution of the crude acid with lead or barium acetate, substances are obtained that become crystalline on standing, the sooner the more dilute the original solution. Either of these precipitates treated with excess of hydrochloric acid, evaporated to dryness, and exhausted with ether, gives on distillation of the ether, a crystalline acid which is purified by recrystallisation from water from small adherent quantities of a yellow viscid substance.

Carius (Ann. Ch. Pharm. cxxvi, 205), by the action of chlorine and mercuric oxide on barium citraconate, obtained an acid which he described as solid, colourless, and uncrystallisable. On repeating his experiments, using sodium citraconate instead of the barium salt, and pursuing the above method of purification, Gottlieb finds that a crystalline acid is obtainable, and that Carius's acid, *monochlorocitraconic acid*, is identical with that prepared by the action of potassium chlorate and hydrochloric acid, or by the other methods above described. At  $100^\circ$  the acid melts to a viscid colourless mass, which solidifies to a

\* Zeitschr. f. Chem. [2], v. 17.



glass on cooling, and does not become crystalline. It is sensibly volatile at common temperatures, and more so at  $100^{\circ}$ . The crystals are anhydrous, but very deliquescent, and seemingly belong to the rhombohedral system. The acid dried over sulphuric acid, or heated to  $100^{\circ}$ , has the composition  $C_6H_7ClO_6$ , two hydrogen-atoms being replaceable by metals. The silver, barium, and lead salts of this composition have been analysed, the two latter crystallising each with  $2H_2O$  and with  $4H_2O$ .

When the barium salt is boiled with baryta water, or even heated therewith to temperatures below  $100^{\circ}$ , a considerable effervescence from the production of carbon dioxide ensues, and ultimately the whole of the chlorine is removed, forming barium chloride. The lead salt behaves in the same way. Carius considers that citratartaric acid,  $C_6H_8O_6$ , is formed by the action of baryta. The author is investigating this reaction.

C. R. A. W.

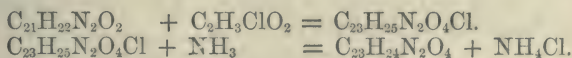
**On the Time required for the Dissociation and Reproduction of Ammonium Carbamate.** By A. NAUMANN (Deut. Chem. Ges. Ber. 815—888. Compare also this Journal [2], ix, 1195).

THE time required for these phenomena depends partly on the quantities of undecomposed salt present, and becomes the shorter the larger the surface of the latter is. When during dissociation, as well as during reproduction, the tension approaches the point of equilibrium, it increases or decreases the more slowly the nearer it comes to that point. The long time required for dissociating or re-forming this compound points out that it is an atomistic and not a molecular combination. It resembles in this respect methyl metaldehyde,  $C_3H_6O_3$ , which, as Hofmann has shown, splits up on heating into three molecules of methylaldehyde, which gas on cooling is slowly transformed again into the solid polymolecular compound.

C. S.

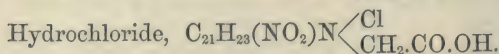
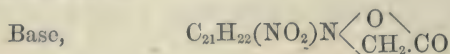
**On a new Base from Strychnine.** By A. STRECKER (Deut. Chem. Ges. Ber. iv, 821—822).

ON heating 3 parts of finely powdered strychnine with 1 part of chloroacetic acid to  $180^{\circ}$  for some hours, dissolving in water, and adding excess of ammonia, some unaltered strychnine separates, whilst the filtrate contains the new base, which on evaporation is obtained in form of white, silky, fascicular needles, readily soluble in hot water and alcohol, but not in ether. The solution has a neutral reaction. The formation of this compound is explained by the equations—



The nitrate and oxalate are very sparingly soluble in water. The solution of the base gives with potassium chromate a yellow crystalline precipitate, and with silver nitrate a silver compound crystallising in long colourless needles. It is also precipitated by bromine-water and

tannic acid. With potassium chromate and sulphuric acid it gives the strychnine reaction. Subcutaneous injections of it produce tetanus in frogs. The constitution of this base and its hydrochloride may be expressed as follows:—



C. S.

**Contributions to our Knowledge of the Cinchona Barks.** By  
O. HESSE (Deut. Chem. Ges. Ber., iv, 818—820).

To distinguish between genuine and false cinchona barks, Grahl heats a small piece in a test tube, which is held horizontally; the genuine barks yield a carmine-red tar, but not the false barks. Batka has shown that this red product is always formed, when a cinchona base is heated with cellulose, and this test is therefore very well adapted to prove the existence of alkaloids in the bark; but it cannot be used as a means of distinguishing between genuine and false barks; because as the author has found, there exist genuine barks containing no bases, and false barks in which alkaloids are present. Thus a genuine bark in his collection (probably from *Cinchona pubescens*) does not contain a trace of any alkaloid, whilst a false bark, which was formerly often found amongst the "soft bark" (*Cinchona lancifolia* var. *obovata*), and is now found in larger quantities in the market, gives the above reaction, because it contains cinchona-bases. This bark, which Flückiger calls *China cuprea*, has a fine red colour, and gives with ammonia a purple solution, which imparts to filter paper a fine pink colour, after exposure to the air. Nitric and sulphuric acids produce in this solution an amorphous reddish brown precipitate. On filtering, a yellow solution is obtained, which, on adding ammonia, assumes a violet colour, and after some time, purple, amorphous flakes separate out, no doubt a product of decomposition of the tannic acid of the bark. This tannic acid is different from that contained in genuine barks, and in *China nova*, as it gives an intense green colouration with ferric chloride. Milk of lime gives with the bark a deep yellowish-red solution, from which, on exposure to the air, a red lime-compound (cinchona-red lime?) separates. On adding an excess of acetic acid to the filtrate, a gelatinous precipitate is obtained, which cannot be distinguished from that which the genuine barks give under the same circumstances. On filtering from this precipitate and adding basic lead acetate, a copious precipitate of basic lead quinate is formed. The following percentage of bases are contained in this bark:—

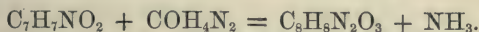
	1.	2.	3.	4.
Quinine.....	1.33	1.28	1.20	1.26
Conchinine (?) ....	—	—	0.46	0.28
Cinchonine .....	—	—	0.22	0.24
Amorphous bases....	—	—	0.37	0.37

The amorphous bases gave the same reaction as quinoidine; quinidine and parisine could not be found.

C. S.

**On the Ethylic Ethers of Uramidobenzoic and Carboxamido-benzoic Acid.** By P. GRIESS (J. pr. Chem. [2], iv, 292—297).

By carefully melting together urea and amidobenzoic acid, uramidobenzoic acid is formed—



The uramidobenzoic acid is gradually converted into carbamidobenzoic acid at 20°—



Hence by this method of preparation a mixture of the two acids is obtained, the relative quantities depending on the time and temperature.

By heating amidobenzoic ether with urea, the ethers of both the above acids are obtained. From this mixture uramidobenzoic ether may readily be extracted by hot water. It melts at 176°. The carbamidobenzoic ether melts at 162°.

On the large scale, uramidobenzoic ether may be obtained by adding hydrochloric solution of amidobenzoic ether to aqueous solution of potassium cyanate.

This ether is identical with the one obtained by the method given above; and the carboxamidobenzoic ether obtained from it by the action of heat, is identical with that mentioned above.

These two ethers may also be obtained by the action of cyanic acid upon alcoholic solution of amidobenzoic acid. A compound is thus formed which, according to analysis, has the formula,  $\text{C}_{20}\text{H}_{30}\text{N}_4\text{O}_9$ . By evaporation *in vacuo* over sulphuric acid, it loses 3 molecules of water, becoming  $\text{C}_{20}\text{H}_{24}\text{N}_4\text{O}_6$ , or, according to the author,  $2\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_3$ , a compound isomeric with uramidobenzoic ether, into which it is converted by the application of heat.

C. C.

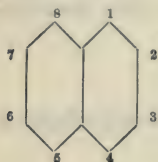
**On Aceto-naphthylamide and some of its Derivatives.** By P. ROTHER (Deut. Chem. Ges. Ber., iv, 850—853).

By heating equal weights of naphthalene and glacial acetic acid together for several days, the author obtained aceto naphthylamide ( $\text{C}_{10}\text{H}_7\text{NH.C}_2\text{H}_3\text{O}$ ), a crystalline body, which melts at 159°. It dissolved readily in cold fuming nitric acid. On adding water to this solution, a yellow mass was precipitated, which, after purification, was shown by analysis to be dinitraceto-naphthylamide ( $\text{C}_{10}\text{H}_5(\text{NO}_2)_2\text{NH.C}_2\text{H}_3\text{O}$ ).

By passing bromine through acetonephthylamine suspended in carbon bisulphide, a heavy amorphous product was formed; according to analysis, monobromacetonephthylamide ( $\text{C}_{10}\text{H}_6\text{Br.NH.C}_2\text{H}_3\text{O}$ ); which melts at 94°. By boiling this product with strong solution of potash,



it was converted into monobromonaphthylamine ( $C_{10}H_6Br.NH_2$ ). This monobromonaphthylamine was converted into the diazo-compound, from which monobromonaphthalene was obtained by heating with alcohol. The boiling point of this compound ( $277^\circ$ ), the melting point, and the crystalline forms of its derivatives, showed it to be identical with the monobromonaphthalene obtained by the direct action of bromine on naphthalene.



From these results the author was led to consider the question of the constitution of isomeric monosubstitution-products of naphthalene. Wichelhaus has shown (*Ann. Ch. Pharm.*, clii, 313) that in  $\alpha$ -naphthol, in the naphthylamine from which it is derived, and in all the  $\alpha$  derivatives, the substituting group is remote from the carbon-junction, viz., at 2, 3, 6, or 7; whereas, in the  $\beta$  derivatives it is near the carbon-junction, viz., at 1, 4, 5, or 8.

Since the bromonaphthalene obtained from bromonaphthylamine is identical with that formed by the direct action of bromine, the group ( $NH_2$ ) of the bromonaphthylamine being at 2, the bromine must be at 3, 6, or 7; the ( $NH_2$ ) being at 1, the bromine must be at 4, 5, or 8. In order to determine the relative positions of the Br and  $NH_2$  in bromonaphthylamine, the author prepared di-bromonaphthalene from diazo-bromonaphthalene (in the usual way), intending to oxidize the di-bromonaphthalene with nitric acid. If by this oxidation he obtained a monobrominated acid, he would infer that the bromine-atoms of the dibromonaphthalene (and consequently the bromine and  $NH_2$  of the bromonaphthylamine) belonged to different benzene nuclei; if a dibrominated acid, that both belonged to the same benzene nucleus. In the latter case the position of the bromine-atoms can only be at 1 and 4, or 2 and 3. To determine this position, he proposes to distil the dibrominated acid with lime, whereby he expects to obtain a dibrominated benzene, and compare it with the dibrominated benzene of Meyer, in which the position of the bromine-atoms is considered as being at 1 and 4.

C. C.

### Preparation of Neutral Sulphate of Eserine (Calabar Bean).

By A. PETTIT (*J. Pharm.* [4], xiv, 255).

THE hydro-alcoholic extract of the Calabar bean (*Physostigma venenosum*) is dissolved in a small quantity of distilled water, and filtered. To the filtrate is added 1 gram of potassium bicarbonate for every 20 grams of extract dissolved, and the solution is agitated with a considerable quantity of ether. After allowing the ether to separate, it is decanted, and the aqueous liquid again treated with ether, until the whole of the alkaloid is completely removed. The ethereal solution, after the addition of a little distilled water, is carefully neutralised with dilute sulphuric acid, containing 40 grams of the monohydrated acid per litre, the point of saturation being ascertained by the aid of good litmus paper. The ether is then gently evaporated or decanted, and the solution of sulphate of eserine concentrated to crystallisation. The first crop of crystals is sufficiently pure for medicinal use, but it is pre-

ferable to treat the alkaloid again with alkali and ether, which, after a second crystallisation, will render the salt perfectly white and pure.

In preparing a solution of the alkaloid, if as many grams of liquid are obtained as it was found necessary to employ drops of the standard sulphuric acid, 1.0 gram of the solution will contain 0.01 gram of eserine. For general purposes, one part of the above solution may be diluted with 4 or 5 parts of distilled water.

J. W.

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## Physiological Chemistry.

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**On a New Method of preparing Glycogen.** By E. BRÜCKE  
(Wien. Acad. Ber., lxiii, [2], 214—222).

THE chief difficulty in the preparation of glycogen in a state of purity consists in the fact that heat alone is not sufficient to coagulate and separate all the nitrogenous substances capable of being precipitated by alcohol. Brücke has found that the nitrogenous substances can be completely precipitated by a solution of potassio-mercuric-iodide. The solution is prepared by precipitating corrosive sublimate with potassium iodide, washing the precipitate, and redissolving it in a hot solution of potassium iodide to saturation.

In order to obtain pure liver-glycogen, the fresh liver is to be thrown into boiling water and briskly boiled for a short time. It is then to be taken out, rubbed down in a mortar, returned to the hot water, and boiled again. The mass is then to be filtered, and the filtrate cooled rapidly by placing the vessel in cold water or snow. After cooling, hydrochloric acid and potassio-mercuric iodide solution are to be added, alternately, as long as any precipitate forms. The mixture is then to be well stirred, and allowed to stand for five minutes or so, and then filtered. To the filtrate alcohol is to be added until a copious deposit of glycogen forms. No excess is to be added, lest any other substances be precipitated, while glycogen is precipitated by even dilute spirit. The glycogen is then to be thrown on a filter and washed, at first with dilute, and then with strong alcohol of 90 per cent., by which means the glycogen is rendered easily separable from the filter. In order to render the glycogen still more pure, it is to be next extracted with ether. Glycogen so obtained is quite free from nitrogen and ash. It is turned red, not brown, by solution of iodine. The red colour is always best marked if the glycogen has not been thoroughly dried. An excess of the reagent is to be avoided. The iodine-solution for this reaction is best prepared by shaking metallic iodine with water, and adding potassium iodide in small quantities till the liquid assumes a wine-yellow tint. In the spectroscope, glycogen exhibits a general absorption, weakest in the red. It turns the plane of polarisation to the right. The solutions of pure glycogen are admirably adapted for demonstrating the colours of turbid media.

By the above method, the quantity of glycogen can be estimated.

In this case, the difficulty is to determine exactly how much alcohol is to be added for the precipitation of the whole of the glycogen, and nothing more. Brücke found that the most correct results are obtained when alcohol is added in the proportion of 60 per cent. of the whole volume, and the precipitate washed with a mixture of alcohol and glacial acetic acid. In this way, all loss of glycogen is avoided. The processes of solution and precipitation of glycogen seem to consist merely in a swelling up and shrivelling of small particles. That the apparent solutions are really only suspensions of swelled up particles is shown by the opalescence of even dilute solutions of glycogen, and by their polarisation of light.

From muscle, glycogen can be prepared in a similar manner to the above. In order to obtain the muscle finely comminuted, a convenient method is to rub it in a mortar with heated coarse lapidary's sand. Or the finely minced muscle may be boiled in sodium carbonate, or in caustic potash. The last method seems best adapted for the quantitative determination of glycogen in muscle, as glycogen seems to be entirely unacted on by this reagent. This, however, will require more careful investigation.

The process for the separation of glycogen may also be employed for the preparation of dextrin free from nitrogenous substances.

Whether glycogen exists in the blood has been much disputed. Sanson finds it in appreciable quantity, while Nasse not only denies the existence of glycogen in blood, but likewise of all amylaceous or dextrin-like substances. Brücke succeeded in demonstrating the presence of very small quantities of a substance giving a red colour with iodine-solution, but he could not obtain it in sufficient quantity to determine whether it was glycogen or dextrin.

With regard to the spleen, the same differences of opinion prevail as in the case of the blood. Brücke obtained a distinct glycogen reaction from the spleen. This he attributes to the muscular fibres of the vessels. In the kidneys also he succeeded in demonstrating minute quantities of glycogen. In the case of the mammary gland, only very doubtful indications of glycogen could be obtained. This quite disproves the theory that glycogen is stored up in the gland preparatory to the formation of milk-sugar.

D. F.

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**On Tissue Change during Fasting.** By J. SEEGEN (Wien. Acad. Ber., lxiii [2], 429—438).

In this paper Seegen gives the results of several observations on the excretion of urea during a period of almost complete starvation, which he had an opportunity of making on a young woman aged 24. Her appetite had been gradually diminishing for some time, and a hardness was observed over the cardiac orifice of the stomach. At length a tumour, the size of a walnut, could be felt at this point, and she became unable to take any food, except small quantities of milk, on account of the pain and vomiting it occasioned. In six weeks after



she had been reduced to live on milk alone, the swelling diminished, and she again became able to enjoy other food. The observations were begun after the patient had been taking very little food for several weeks, and for nearly 14 days had been living on 35 grams of fresh milk daily. For the first 12 days during which they were made, her daily food consisted of 35 grams of milk mixed with 20 c.c. water. On one of these days, instead of milk, she took the white of an egg, and on another a whole egg.

The 35 grams of milk would contain, according to the determination of Becquerel and Vernois, 1.9 gram of albumin, corresponding to 0.29 gram of nitrogen taken daily, or 3.4 in 12 days. The urea excreted during the same period amounted to 106.9 grams containing 49.8 grams of nitrogen, and the excess of nitrogen, excreted over that consumed, and which necessarily must have come from the transformation of the tissues of the body, was 46.4 grams. This would correspond to 299.3 grams albumin consumed in 12 days, the consumption of albumin in the body was therefore almost 25 grams daily.

The amount of water excreted in the urine was 223.0 c.c. during 12 days, or 185 c.c. per diem. The amount drunk daily was only 55 c.c., and therefore 130 c.c. were daily excreted at the expense of the body. On the assumption that the nitrogen excreted was derived from muscle, and that muscle contains 75 per cent. of water and 3.4 per cent. of nitrogen, the amount of muscle which underwent transformation daily, would be 112 grams. This would yield only 84 c.c. of water, and leaves 56 c.c. to be accounted for. A considerable quantity of water also leaves the body by the skin and lungs in addition to that excreted by the kidneys. The tissues must, therefore, become poorer in water.

The amount of water and urea excreted was not the same on each day. The mean daily excretion of urea was 8.9 grams.

From the 13th day of observation onwards to the 24th, a much larger quantity of food was taken, the milk during these 11 days amounting to 2275 grams, besides an egg, or a little arrowroot occasionally.

The nitrogen taken into the body during this period in the milk alone was 1.76 gram daily, while in the first 12 days it was only 0.2 gram.

The daily excretion of nitrogen, however, was only 0.37 gram in excess of the daily excretion during the first 12 days.

The excess of nitrogen taken in the food during the second period over that in the first, was therefore not excreted, but stored up in the body.

The excess of water in the second period was all excreted in the urine. A comparison of the results of this research with those of other experiments formerly made by the author on well-nourished persons, shows that the organism, when deprived of food and living at the expense of its own tissues, consumes  $\frac{1}{3}$ th of the albumin which would undergo transformation in a normally nourished person. No general rule can, however, be deduced from one experiment, and the small amount of tissue-change observed in the present instance, as compared with that noticed by others in their experiments on animals was pro-

bably due to the body in this case resting in bed, and making little movement.

T. L. B.

### Agricultural Chemistry.

#### On the Distribution of Potash and Soda in Plants. Part IV. By E. PELIGOT (Compt. rend., lxxiii, 1072—1080).

THE author's views on this subject have been already fully given.\* He mentions an additional experiment, supporting his opinion that soda is not a universal constituent of plants, but is characteristic of certain plants only. A beet-root was grown in the middle of a bed of parsnips; the ash of the beet-root yielded soda in distinct quantity; the parsnips around it contained no soda either in leaf or root. The author believes that the value of common salt as a manure has been greatly overrated. Where it has a beneficial influence on crops other than beet-root, &c., it is possibly owing to its solvent power for calcium phosphate.†

Analyses of soil from the polder land, in the Bay of Bourgneuf, are given. The soil now contains 60—600 milligrams per kilogram of soluble chlorides, a quantity not greater than that of inland soils. Eight years previously, when the land had been reclaimed from the sea only one year, the amount of salt in two cases was 1·76 and 6·5 per cent. In proportion as the salt has been washed out by rain and removed by suitable drainage, the fertility of the land has risen.

R. W.

#### Note on "Le Salant." By E. P. BÉRARD (Compt. rend., lxxiii, 1155—1158).

"LE SALANT" is the name given to a saline incrustation which appears on the surface of the soil in certain districts in the south of France, especially after long drought, and occasions complete sterility. The author examined samples of this incrustated soil obtained from the very fertile plain of Agde, Hérault. The soil here is a deep alluvial deposit, periodically flooded by river water. The watery extract from 100 grams of soil contained as follows:—

	Surface soil.	The same soil. Depth 30 cm.	Another surface soil.
Sodium chloride .....	6·163	·761	·845
Magnesium sulphate .....	·228	·129	·300
Calcium sulphate.....	·176	·051	—

The incrustations are very local. A field adjoining the first soil was exceedingly fertile, and contained but ·05 per cent. of sodium chloride.

\* See page 851 of the last volume.

† A far more important action of salt is suggested by Dr. Voelcker. Jour. Roy. Agri. Soc. [2], i, 298.

The efflorescence is supposed to be derived from beds of saline matter within the soil, the existence of which is, however, not proved. The remedies for sterility consist in drainage and operations tending to increase the porosity of the soil.

R. W.

**Quantities of Nitrous and Nitric Acid in Rain Water.** By CHABRIER (Compt. rend., lxxiii, 485—488).

THE author has chiefly examined rain waters collected at St. Chamas, Bouches-du-Rhône. The rain-fall in this district is about 5,100,000 litres per hectare (about 20 inches), with an average of 50 rainy days in the year. The first ten of the following analyses are of water from this locality. The results are given as milligrams per litre.

Date of collection.	Observations.	Nitrous acid.	Nitric acid.
1870.			
Jan. 22 ....	Wind N., ozone paper* 18° .....	·295	·007
Jan. 31 ....	Heavy rain, wind N.E., ozone paper 15°—17° ..	·154	·005
Feb. 3 .....	Some thunder, wind E. to N., ozone paper 19° ..	·857	·026
Feb. 5 .....	Wind N.E., ozone paper 20° .....	·782	·039
March 29 ..	Fine rain, wind N.W., ozone paper 16° .....	·836	·029
April 7 ....	Wind N.E., ozone paper 12°—17° .....	None.	2·763
June 6.... {	Heavy rain after drought, wind N., ozone paper 7°—15° .....	None.	·746
June 7.....	Little rain, wind N.E., ozone paper 12°—17° ..	·312	·830
June 9.....	Heavy rain, wind N.E., ozone paper 14°—17° ..	·154	1·159
July 12 ....	.....	·219	·653
1871.			
March 17 ..	Snow from Langres .....	·732	3·400
April 11 ....	From St. Chamas .....	·690	—
1869.			
Jan. 8 .... {	From Constantine, Algeria, analysed after two years .....	·987	2·750

The author concludes that ammonium nitrite predominates in rain water during the early months of the year, and that little ammonium nitrate is then present.

R. W.

## Analytical Chemistry.

**Detection of Hydrochloric Acid in cases of Poisoning.** By J. BOUIS (Compt. rend., lxxiii, 1109).

WHEN small quantities only of hydrochloric acid can be detected in the contents of the stomach, it is often difficult to decide whether a poisonous dose has been administered or not, inasmuch as minute quan-

\* The scale of the ozone paper was 0°—21°.



tities of the acid alluded to are invariably present in the natural and healthy stomachic juices. In addition to this, the author finds that the processes commonly adopted to effect the isolation of free acid, or to demonstrate its presence by the evolution of chlorine gas, are generally unsuccessful, owing to the large proportion of organic matter present; he therefore advises that the direct evidence of poisoning by hydrochloric acid should rest upon the solubility of gold-leaf in the liquid obtained by heating the contents of the stomach with addition of a small quantity of potassium chlorate. The operation is conducted as follows:—

The contents of the stomach to be tested are first filtered through paper or fine muslin previously moistened with acetic acid. To the filtered liquid gold-leaf is added, and afterwards a few grains of potassium chlorate. The mixture is then heated on a water-bath for two hours, filtered, and afterwards tested with stannous chloride to ascertain if gold has been dissolved. If such be the case, the presence of free hydrochloric acid may with certainty be relied upon, provided, of course, that proper precautions have been taken to ensure the absence of nitric and sulphuric acids.

When the liquors are very dilute, they should be evaporated to at least one-half upon the water-bath, in presence of gold and potassium chlorate. In this manner even a few centigrams of hydrochloric acid may be detected, when diffused through a large volume of a very complex liquid.

The author has assured himself that a mixture containing both potassium chlorate and sodium chloride in solution has no action upon gold, either when boiled alone, or with lactic or acetic acid.

J. W.

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**On Hydrometry and the German Scale of Hardness.** By  
E. REICHARDT (*Zeitschrift für Anal. Chemie*, x, 284—292).

THE author considers the usual method of estimating the hardness of a water by means of soap-solution to be unsatisfactory. He cites the results obtained by various chemists. Thus Clark gives 1.7—2.2 cub. cents. of soap-solution as equivalent to 1 degree of hardness; and Campbell states that a mixture of lime and magnesia requires less soap-solution than an equal quantity of pure lime or pure magnesia.

Faist, Knauss, and Wilson state that, with a mixture of lime and magnesia, 2 cub. cents. = 1 degree hardness. Schneider, who controlled his results by gravimetrical analyses, finds that the soap-solution method is only to be depended on when, besides lime, but very small quantities of magnesia are present, and also that the amount of lime itself must be large.

The author considers the German method of precipitating separately the lime, magnesia, sulphuric acid, and chlorine to be the only perfectly trustworthy one.

T. E. T.

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**Estimation of Ammonia in presence of Soluble Phosphates by means of Calcined Magnesia.** By MAX MÄRCKER (*Zeitschrift für Anal. Chemie*, x, 277—280).

A METHOD for the estimation of ammonia, by boiling with calcined magnesia and absorbing the gas by standard sulphuric acid, is often employed in the case of certain organic substances, as ground bones, horns, &c., which do not contain all their nitrogen as ammonia salts, and moreover, contain notable quantities of phosphates. Doubt has lately been thrown on the trustworthiness of this method. The author gives the results of several determinations, which tend to show that as much ammonia is given off by boiling with calcined magnesia, as with stronger alkalis, caustic potash, or milk of lime; and also that the presence of soluble phosphates does not interfere with the ammonia estimation.

T. E. T.

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**Estimation of Phosphorus and Sulphur in Iron.** By K. MEINEKE (*Zeitschrift für Anal. Chemie*, x, 280—284).

THE author points out the uncertainty attaching to most methods of estimating phosphorus and sulphur in specimens of iron. He proposes a modification of the method of Gintl, who decomposes the iron by ferric chloride, in place of which the author substitutes cupric chloride.

5 grams of iron in fine powder are decomposed in from 1 to 1½ hours by gentle warming with a concentrated solution of cupric chloride. After carefully decanting off the iron solution, the separated copper is removed by renewed addition of cupric chloride, cuprous chloride being formed, which is kept in solution by adding common salt.

The insoluble residue is separated by means of an asbestos filter, washed, thrown with the filter into a beaker, oxidised with strong nitric acid and chlorate of potassium, evaporated to dryness, and in the solution therefrom sulphur is estimated as barium sulphate. To the filtrate ammonia is added, which precipitates iron oxide along with the phosphoric acid; this precipitate is dissolved in hydrochloric acid, and the phosphoric acid estimated by a molybdic acid solution.

The author's results show a somewhat higher percentage of sulphur than results obtained by the older process of driving off the sulphur as sulphuretted hydrogen, taking it up in an ammoniacal silver solution, and estimating the sulphur in the silver sulphide formed. He thinks his analyses go to prove that, in using the old process, there always remains a certain amount of sulphur, not driven off as sulphuretted hydrogen. If phosphorus only is to be estimated, the insoluble residue together with the separated copper is washed, oxidised as formerly, evaporated to dryness with hydrochloric acid, water added, and then ammonia. There is always so much iron oxide present, that all the phosphoric acid is precipitated. In the hydrochloric acid solution in which the precipitate is re-dissolved, phosphoric acid is estimated by a molybdic acid solution.

T. E. T.

**Estimation of Iron and Ferrocyanogen.** By H. RHEINECK  
(Dingl. Polyt. J., ccli, 154—159).

THE estimation of ferrocyanogen in potassium ferrocyanide, Prussian blue, and other metallic ferrocyanides, by converting it into ferricyanogen by the action of oxidising agents, as permanganic acid or alkaline hypochlorites, suffers from the defect, that it is difficult, in fact almost impossible, to complete the reaction, because, when the solution is much diluted, the ferrocyanide is not affected by the oxidising agent. Moreover, the method is inapplicable in the case of solutions containing other oxidisable bodies.

To avoid these inconveniences, the author adopts a volumetric method founded on the formation of Prussian blue by the mutual action of ferric salts and ferrocyanides, the completion of the reaction being determined as follows:—

When to a solution of potassium ferrocyanide, with or without the addition of a mineral acid, a ferric solution is slowly added, the blue precipitate at first formed disappears again, the solution remaining blue and clear; on further addition it becomes muddy, but still always preserving its character as a blue solution, till suddenly a drop more iron solution causes sudden coagulation, the liquid soon separating into a clear colourless layer, and the blue flocculent precipitate settling to the bottom. In the clear solution neither iron nor ferrocyanogen is present.

The author gives in detail the results of a number of quantitative volumetric experiments, in which he used potassium ferrocyanide and ferric solutions of known strength, the sudden coagulation of the solution, as above described, being taken as the indication of the completion of the reaction.

It was found that, in order to obtain concordant results, it was necessary to observe the following precautions, viz.:—The solution of the ferrocyanide must be, to a certain extent, diluted with water, or the reaction denoting the completion of the experiment, will be obtained too soon, *i.e.*, the quantity of ferric solution required to attain this point will be less than that which is equivalent to the ferrocyanogen present. It was found also that the addition of acid is requisite even when the above precaution is observed.

The ferrocyanogen in a sample of yellow prussiate may also be determined quickly and with certainty by this process.

It was found that a dilute solution of potassium ferrocyanide soon altered in strength and became darker coloured, but a stronger solution (a 10 per cent. solution) was kept unaltered for several months.

Finally, the author applies the principle of his process to the estimation of certain other metals which furnish insoluble ferrocyanides, viz., uranium, copper, and lead. In the case of the uranium and copper he obtains satisfactory results.

W. S.



**Estimation of the Strength of Bleaching Powder.** By  
DR. GRAEGER (Dingl. Polyt. J., cci, 162).

THE author, in searching for a simpler process for the valuation of bleaching powder than those of Penot and R. Wagner, has hit upon the following method, which he considers to possess the required advantage:—

To a dilute and strongly acidified solution of ferrous sulphate, of which the titre is exactly fixed with  $\frac{1}{10}$  potassium permanganate solution, the bleaching powder solution is added by the pipette, the point of the latter being placed close on the bottom of the vessel, so that the bleaching powder solution forms the lower layer of liquid; the glass stopper is placed in the flask, and the latter, with its contents, is well shaken, and then allowed to stand some minutes. When a sufficient quantity of ferrous sulphate is used, scarcely any smell of chlorine—in most cases, none at all—is perceived on opening the flask. The excess of the ferrous salt is now estimated with the  $\frac{1}{10}$ th permanganate solution, the difference between this and the original amount of ferrous salt used representing the weight oxidised by the hypochlorous acid, from which the available chlorine in the powder is readily calculated. If 1 gram of bleaching powder be fixed as the constant weight to be taken, a sufficient excess of iron salt must be taken to absorb all the oxygen yielded, and to leave a not too large residue to be estimated by the permanganate solution. The author recommends 4 or 5 grams of ferrous sulphate as the weight to be used. The results were found to correspond exactly with those obtained by the use of Penot's solution of sodium arsenite. The author claims for his process the possibility of executing experiments by its use with greater speed, and with equal accuracy to those obtained by any other method. He does not recommend the use of ammonio-ferrous sulphate as a substitute for ferrous sulphate, since nitrogen chloride is formed, as previously shown by Biltz.

W. S.

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## Technical Chemistry.

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### On the Calorific Value and Composition of two Welsh Coals.

By A. SCHEURER-KESTNER and CH. MEUNIER (Compt. rend., lxxiii, 1061).

Two samples of Welsh coal were examined. The first, from Bwlf, contained 3.32 per cent. ash, and gave 82.08 per cent. of coke; its calorific value was 8780 units. Allowance being made for ash and water, its composition was—carbon, 91.08 per cent.; hydrogen, 3.83 per cent.; oxygen, 5.09 per cent.

The second, from Mr. Powel, contained 3.72 per cent. of ash, gave 81.16 per cent. of coke, and had a calorific value of 8949 units. Its composition, allowing for ash and water, was—carbon, 92.49 per cent.; hydrogen, 4.04 per cent.; oxygen, 3.47 per cent.

The carbon in the two coals was distributed as follows:—

	Coal from Bwl.	Mr. Powel's Coal.
Carbon in the hydrocarbons.....	9.07	5.14
Fixed carbon.....	82.01	87.35

The two samples of coal thus differ considerably in their constitution, although their ultimate composition is not materially different.

The following are the general conclusions arrived at by the authors:—

1. The calorific value of a coal depends more on its constitution than on its ultimate composition.

2. The calorific value of a coal is higher than the sum of the calorific values of its constituents (as shown by an examination of 21 different samples of coal).

3. The calorific value of a lignite is less than the sum of the calorific values of its constituents.

4. The calorific value of pure cellulose is equal to the sum of the calorific values of its constituents.

A. D.

**On the so-called Scott's Cement.** By FRIEDRICH SCHOTT  
(Dingl. polyt. J., ccli, 52—76).

CAPTAIN H. Y. D. Scott pointed out, in the year 1854, that quick lime heated to redness in the vapours of burning sulphur lost its power of slaking, but acquired hydraulic properties, gradually hardening when stirred up in water. The present author has examined the mode of formation of the cement, with the view of determining the nature of the compound formed, and the best way of producing it. His principal results are: that cold dry lime does not absorb cold dry sulphurous acid, but that at a red heat it absorbs the gas completely, without evolution of any gas; that when sulphurous acid gas is passed over red hot lime contained in a tube, combination takes place, with evolution of heat and light, forming a mixture of sulphate and sulphide of calcium, with excess of lime in uncertain proportions. That when sulphite of calcium is heated to a moderate red heat, it decomposes thus:— $4\text{CaSO}_3 = 3\text{CaSO}_4 + \text{CaS}$ , forming a mass devoid of hydraulic properties; but when heated to whiteness it sinters, leaving a mass containing only about half the sulphur required by the above formula, and capable of hardening under water.

Thus a mass having all the properties of Scott's cement, can be prepared by *strongly igniting* a mixture of gypsum and lime, in the proportion of 2 molecules of sulphate of lime to 3 molecules of lime. The cement so formed is the better the higher the temperature at which it has been formed, and the less sulphide of calcium it contains.

C. H. G.

## PAPERS READ BEFORE THE CHEMICAL SOCIETY.

## IV.—COMMUNICATIONS FROM THE LABORATORY OF THE LONDON INSTITUTION.

No. IV.—*The Nitration-products of the Dichlorophenolsulphonic Acids.*

By HENRY E. ARMSTONG.

I HAVE previously stated that when ordinary dichlorophenol is converted into sulpho-acid by digestion with sulphuric acid, and the product is submitted to the action of nitric acid, Stenhouse's dinitrochlorophenol (melting point  $103^{\circ}$ ) is obtained. This observation seemed necessarily to lead to the conclusion that the dichloro-sulpho-acid so formed is isomeric with those obtained by direct chlorination of Kekulé's meta- and para-phenolsulphonic acids, which yield dichloro-nitrophenols, melting respectively at  $121.5^{\circ}$  and  $125^{\circ}$ , corresponding to dinitrochlorophenols melting at  $80.5^{\circ}$  and  $111^{\circ}$ .

The action of sulphuric acid on dichlorophenol had furnished but a poor yield of sulpho-acid, and as I required a considerable quantity of the latter, in order to study its transformations, I was led to substitute chlorhydric sulphate,  $\text{SO}_2\text{OHCl}$ , for dihydric sulphate,  $\text{SO}_2(\text{OH})_2$ , hoping thereby to obtain an increased, if not theoretical, yield of sulpho-acid.

$\text{SO}_3\text{HCl}$  (1 mol.) was added gradually to dichlorophenol (1 mol.) diluted with a small quantity of carbon bisulphide. The action was immediate, and volumes of hydrochloric acid escaped. The carbon bisulphide was subsequently distilled off, the product digested for about an hour on the water-bath, and after cooling poured into cold water. Nearly the whole dissolved, a proof that the conversion into sulpho-acid was almost complete. Sufficient potassic carbonate was then added to form the potassic salt, and the solution was evaporated to dryness. The potassic salt so obtained, though readily soluble in hot, is difficultly soluble in cold water, from which it separates in groups of short, opaque, white needles.

The dry sulpho-salt was then acted on by nitric acid (1.36) in the cold, and the nitro-product subsequently converted into potassium derivative, and fractionally crystallised. Thus was obtained, as sole product of the reaction, nitrodichlorophenol melting at  $121.5^{\circ}$ , viz., the same body that is obtained by direct nitration of the dichlorophenol from which the sulpho-acid operated upon was prepared. The intro-



duction of the  $\text{SO}_3\text{H}$  group into the complex has, therefore, in this instance, had no influence in the subsequent nitration.

I now proceeded to treat a portion of the same potassic salt with acid at a temperature of  $40^\circ$ — $50^\circ$ , expecting to obtain, as by the nitration of the sulpho-acid prepared by the action of sulphuric acid on dichlorophenol, dinitrochlorophenol, melting point  $103^\circ$ ; this proved not to be the case, however, the same dichloronitrophenol, melting point  $121.5^\circ$ , as before was obtained, and under no circumstances, even by the action of a much stronger acid, and at higher temperatures, was I able to determine the formation of any other than this.

I mentioned in a previous paper that when a mixture of phenolmeta- and phenolpara-sulphonic acids was chlorinated, and the mixed product nitrated, there was obtained—besides the nitro-compounds which could be fixed as derived from the dichlorophenolparasulphonic acid—dichloronitrophenol melting at  $121.5^\circ$ , which was probably the *sole* nitration-product of the dichlorophenolmetasulphonic acid, since no corresponding dinitrochlorophenol was formed. There is now no doubt, I believe, that the above described dichlorophenolsulphonic acid, obtained by the intervention of  $\text{SO}_3\text{HCl}$ , is this same dichlorophenolmetasulphonic acid. I hope to effect its reduction to phenolmetasulphonic acid by nascent hydrogen, and also intend to compare it directly with the chlorination product of pure phenolmetasulphonic acid.

The only possible interpretation of the above anomalous result is, in my opinion, that the sulpho-acids obtained respectively by the action of  $\text{SO}_4\text{H}_2$  and  $\text{SO}_3\text{HCl}$  on dichlorophenol, are *isomeric*, and I am the more persuaded of this by the following facts:—In a former communication, “On the formation of Sulpho-acids,” I described the action of  $\text{SO}_3\text{HCl}$  on several benzene derivatives, and stated how in some cases the substituted sulpho-acid was the sole product, whilst in others a mixture of substituted sulpho-acid and substituted sulphobenzid was obtained. I have since extended this investigation to a number of mono- and di-benzene substitution-derivatives, and have obtained, for instance, from chlorobenzene, dichlorosulphobenzid and chlorobenzene-sulphonic acid, from cyanobenzene (benzonitril) dicyanosulphobenzid, &c., &c., reactions of which I hope shortly to bring a detailed description before the Society. On examining the salts, however, more especially of the chloro- and bromo-benzenesulphonic acids so obtained, I have observed that they all differ somewhat in the amounts of water of crystallisation, &c., from the corresponding salts of the acids obtained by the action of  $\text{SO}_4\text{H}_2$ , as described by Glutz, Otto, Garrick, and others, and without having yet directly compared the bodies from the two sources, or submitted my product to the crucial test of fusion with potassic hydrate, I believe there is sufficient evidence to show that, in many cases at least, the acids obtained by the action of  $\text{SO}_3\text{HCl}$  are

isomeric with those formed by  $\text{SO}_4\text{H}_2$ , the above described difference in comportment of the acids from dichlorophenol being confirmatory of this view. Again, Petersen has described at great length the conversion of monochlorophenol into sulpho-acid by the action of  $\text{SO}_4\text{H}_2$ , and the nitration-products of this sulpho-acid, which are mainly dinitrochlorophenol melting at  $80.5^\circ$ ; ditto, melting at  $69.5^\circ$ ; ditto melting at  $114^\circ$ ; and dichloronitrophenol melting at  $106^\circ$ ; the two latter being formed in small quantity only; in no case was a nitro-chloro-sulpho acid detected, although specially sought for. By converting the same monochlorophenol into sulpho-acid by the action of  $\text{SO}_3\text{HCl}$ , and nitrating, I have obtained totally different products, viz., (1) a nitro-chlorosulpho-acid, distinguished by the insolubility of its potassic salt; (2) dinitrochlorophenol melting at  $103^\circ$ . I have not yet examined this reaction in detail, so reserve further description for the present; it seems, however, to leave no doubt as to the isomerism of my product with Petersen's.

I believe the isomerism of the sulpho-acids formed in the above two ways might almost have been theoretically predicted, when the conditions under which the various substituted phenols are formed are considered. Let us compare the action of the halogens and of nitric acid on phenol, with that of sulphuric acid. The "reactive energy," if I may use the term, of the latter agent is feeble compared with that of chlorine and bromine; by its action on phenol we obtain two sulpho-acids, the so-called *meta*- and *para*-phenolsulphonic acids; by the action of chlorine (Br) on phenol in the cold, two monochlorophenols are formed, by far the larger quantity, however, consists of *ortho*chlorophenol. Similarly by the action of nitric acid, an extremely powerful agent, *ortho*- and *meta*-derivatives are formed simultaneously. The "reactive energy" of the chlorhydric sulphate is far greater than that of sulphuric acid, and it may rather be compared in its action to chlorine than to sulphuric acid, and it seems to me, therefore, that it should give rise to derivatives belonging to a different series to those obtained by the aid of sulphuric acid. In all probability, however, there is a direct relation between the amount of heat evolved in the formation of a substitution-derivative and the position it assumes in the isomeric series. I believe, moreover, that, in the formation of compounds of the so-called *ortho*-series, less heat is evolved than in the production of *para*-derivatives, the *meta*-derivatives probably occupying an intermediate position. On this assumption we can readily understand how it is that such bodies as Cl, Br,  $\text{HNO}_3$ , &c., which effect the replacement of hydrogen with such ease, should preferably form *ortho*- and *meta*-derivatives, whilst I,  $\text{H}_2\text{SO}_4$ , &c., less energetic reagents, should form *meta*- and *para*-derivatives. A direct study of the heat evolved in the formation of *isomeric* bodies will doubtless

throw great light on this subject, and I intend, at the earliest possible opportunity, to prosecute such a series of experiments. It will first be necessary to ascertain the "thermic" relations of the three isomeric series—ortho, meta, and para—and this I propose to do by determining the heats of combustion of the three isomeric dihydroxybenzols, the three phthalic acids, and the three oxybenzoic acids.\*

I have observed that on nitrating crude dichlorophenol, and purifying the resulting nitrodichlorophenol by recrystallisation of the potassium derivative, the mother-liquors always deposit a small quantity of an orange-yellow salt, also the potassium salt of a nitrodichlorophenol, according to analysis, but differing from either of the three already known. The same was obtained on nitration of the sulpho-acid from dichlorophenol by  $\text{SO}_3\text{HCl}$ . This salt crystallises with one molecule of water, and yields, on decomposition with dilute acid, a nitrodichlorophenol melting at about  $95^\circ$ , almost insoluble in water, from which it separates in short pale yellow needles. The quantity hitherto obtained has been so small that I have not been able to characterise it further by the preparation of salts.

*Dinitrochlorophenol—melting point  $103^\circ$ .*

This body has been obtained by Dr. Stenhouse by the action of chloride of iodine on picric acid.† Dr. Griess,‡ by the action of nitric acid on crude chlorinated phenol, prepared by passing a moderately strong stream of chlorine into about 1 lb. of phenol for 15 hours, obtained, among other products, a dinitrochlorophenol melting at  $103^\circ$ , which Stenhouse has assumed to be identical with his product. I believe the following facts, taken together, prove that Griess's product is identical, not with that of Stenhouse, but with the so called  $\beta$ -dinitrochlorophenol melting at  $110^\circ$ — $111^\circ$ .

1.  $\beta$ -dinitrochlorophenol was obtained by Faust and Saame by nitration of crude monochlorophenol, but neither did they nor Fischer ever observe the formation of the  $103^\circ$  melting-point body on nitration of either mono- di- or tri-chlorophenol, nor have I been more successful.

\* The two isomeric succinic acids may be quoted as an extremely interesting case of isomerism proper. Whereas the ordinary acid (from ethylene dicyanide) volatilises when heated, and is finally converted into the anhydride, the isosuccinic acid (from cyanopropionic acid) splits up at quite a low temperature into propionic acid and carbonic anhydride. The amount of heat evolved in the combustion of the latter acid will no doubt be found to be much greater than that evolved by combustion of the extremely stable ordinary acid.

† Journ. Chem. Soc. [2], v, 433.

‡ Ann. Ch. Pharm., cix, 286.



2.  $\beta$ -dinitrochlorophenol, when reduced, yields amido-nitrochlorophenol, crystallising in long *brass-yellow* needles, which contain half a molecule of water, and become *brick-red* when dried at  $100^{\circ}$ , then melt at about  $160^{\circ}$ . Griess's description of the amido-product from his dinitrochlorophenol agrees literally with the above, whereas, as I have found, the amido-product from Stenhouse's phenol forms *bronze-yellow* needles, which also contain half a molecule of water, but become *cinnamon-brown* on drying at  $100^{\circ}$ , and then melt at about  $158^{\circ}$ .

3. The salts obtained from  $\beta$ -dinitrochlorophenol, and from the  $103^{\circ}$  body, differ so slightly, that little weight can be attached to the description given by Dr. Griess of the salts he obtained, as a means of determining the identity of one or the other of the above. On the other hand, he says that the silver salt forms crimson laminae; neither the  $111^{\circ}$  nor  $103^{\circ}$  melting-point phenol gives such a salt; both are yellow; but this discrepancy at once disappears when the assumption is made that Griess's product contained dinitrochlorophenol melting at  $80.5^{\circ}$ , which yields a crimson salt.

4. On application to Dr. Griess, he kindly gave me his small specimen (a fraction of a gram) of his product. I was able to recrystallise this from water, and take its melting-point. In appearance the crystals are not distinguishable from those of  $\beta$ -dinitrochlorophenol, but distinctly *lighter* in colour, and more laminated than the  $103^{\circ}$  body. The melting point was about  $109^{\circ}$ , the same thermometer giving  $110^{\circ}$  and  $103^{\circ}$  respectively as the melting points of  $\beta$ -dinitro- and Stenhouse's dinitro-chlorophenol. The low melting point observed by Griess is readily accounted for by the above assumption that the specimen employed by him contained traces of the isomeride melting at  $80.5^{\circ}$ . This latter being the end-product of the nitration of ordinary monochlorophenol, as shown by Faust and Saame, must have been present in Griess's crude product, inasmuch as, according to my experience, "a moderately strong stream of chlorine" would not suffice to dichlorinate "about 1 lb. of phenol in 15 hours." If then my conviction be true, Dr. Stenhouse discovered a new dinitrochlorophenol, and not merely a new method of describing one already known.

*Trichlorophenolsulphonic Acid*.—Trichlorophenol is readily acted upon by chlorhydric sulphate, with evolution of hydrochloric acid. The product dissolves for the greater part in cold water, but the aqueous solution of the sulpho-acid becomes decomposed on standing, with separation of trichlorophenol.

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V.—On *Eulyte* and *Dyslyte*.

By HENRY BASSETT.

THE substances described in the following note were first obtained by Baup\* in 1851, but he gave no more than an account of their general characters. Thinking it of interest to examine their nature more thoroughly, I commenced the preparation of a sufficiently large quantity for examination.

Citric acid was distilled in quantities of half a pound at a time, the receiver being changed on the appearance of oily drops in the distillate. The oily portion was redistilled, and the product exposed to the air in shallow dishes for a few days, when it became a mass of crystals of citraconic acid, which was drained in funnels, the fluid portion being redistilled. The first watery distillates gave, on concentration, a small quantity of itaconic acid, and by redistillation of the mother-liquor, a further quantity of citraconic anhydride.

The crystallised citraconic acid was then treated with nitric acid of sp. gr. 1.45, using 10 grms. of the former to 15 grms. of the latter—larger quantities were found to cause a too violent reaction.

The mixture was gently heated until action commenced, and the lamp then removed. After completion of the reaction, when most of the nitric acid was decomposed or driven off, the solution deposited an oil, the quantity of which was increased by adding a certain quantity of water. The oil was then washed two or three times with fresh quantities of water. It remains fluid occasionally for days, unless touched with a glass rod, when it crystallises in a short time.

The acid mother-liquor contains a large quantity of oxalic, and some mesaconic acid, the citracartic acid of Baup.

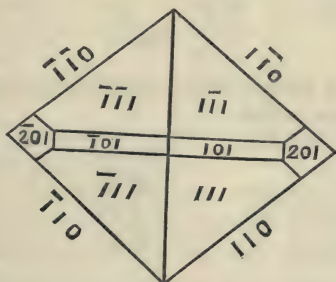
The oily product, the quantity of which is unfortunately very small, consists of a mixture of two neutral crystalline substances, and a small quantity of a yellow oil. The complete separation of these is a matter of considerable difficulty, notwithstanding their great difference in solubility in alcohol, from the fact that the less soluble substance is easily taken up and obstinately held in solution in the presence of the more soluble body, which is the main product of the reaction. However, by numerous fractional recrystallisations, the two solid substances are obtained in a pure state.

The more soluble substance agrees perfectly in character with the *Eulyte* of Baup. It is best crystallised from warm chloroform, which deposits it on cooling in large prisms with very perfect and brilliant faces. Heated with alcoholic potash, it is decomposed, with formation

\* Ann. de Chim. et Phys., xxxiii, 192.

of nitrite, and a brown resin soluble in alkalis. Its melting point was found, from several closely agreeing determinations, to be  $99.5^\circ$  (corrected); its solidifying point is very uncertain, as it occasionally remains fluid for hours, unless touched with a hard body. By very careful heating it appears to sublime unchanged, but at a high temperature it is decomposed, with evolution of nitrous fumes; if in somewhat large quantity with violent combustion.

Through the kindness of Professor W. H. Miller, I am enabled to give the following list of angles, and a figure, a projection of the crystal on a plane normal to the axis.



*Eulyte.*

Prismatic.—Angular elements.

$$\begin{array}{ll} 001, & 101 = 40^\circ 45' \\ 100, & 110 = 49^\circ 39' \end{array}$$

Simple forms—

$$101, \quad 201, \quad 110, \quad 111, \quad 100$$

Angles between normals to the faces—

101,	$\bar{1}01$ .....	$80^\circ 9'$
201,	$\bar{2}01$ .....	$118^\circ 33'$
110,	$\bar{1}10$ .....	$80^\circ 42'$
100,	110 .....	$49^\circ 39'$
100,	111 .....	$59^\circ 8'$
111,	$\bar{1}11$ .....	$61^\circ 44'$
111,	$1\bar{1}1$ .....	$74^\circ 18'$
111,	$\bar{1}\bar{1}1$ .....	$104^\circ 50'$
101,	111 .....	$37^\circ 9'$
110,	111 .....	$37^\circ 35'$

Cleavage: extremely doubtful indications parallel to the faces of the form 110.

The analyses of the substance gave the following results (Nos. I, IV, V, crystallised from alcohol; Nos. II, VI, from chloroform; No. III from alcohol, but different specimen).



I.	·387	grm.	gave	·4155	carbonic acid and	·091	water.
II.	·445	"	"	·477	"	·105	"
III.	·2735	"		49·59	cc. nitrogen, at 0° and 760 mm.		
IV.	·2498	"		44·7	"	"	"
V.	·2773	"		50·23	"	"	"
VI.	·2233	"		39·88	"	"	"

These numbers correspond to the percentages below—

	I.	II.	III.	IV.	V.	VI.
Carbon ....	29·28	29·24	—	—	—	—
Hydrogen..	2·61	2·62	—	—	—	—
Nitrogen ..	—	—	22·77	22·45	22·76	22·43

which agree perfectly with those calculated from the formula,  $C_6H_6N_4O_7$ , as will be seen on comparison—

	Theory.	Exp. (mean.)
Carbon .....	29·27	29·26
Hydrogen .....	2·52	2·61
Nitrogen.....	22·76	22·60

In the hope of obtaining a basic derivative which might throw some light on the question of the constitution of this body, a solution in alcohol was digested for some hours at a moderate heat with tin and hydrochloric acid, saturated when cold with hydrosulphuric acid, filtered from the tin sulphides, and evaporated to dryness on the water-bath. The residue treated with cold water gave a large quantity of chloride of ammonium, as was proved by a platinum estimation, and a brown tarry mass, which, on treatment with potash, dissolved entirely, giving off the characteristic smell of picoline or a similar base. In a previous trial experiment, which was stopped before complete reduction, I obtained indications of the presence of a solid base, precipitated by ammonia but soluble in potash, forming an oily hydrochlorate almost entirely insoluble in cold water but soluble in alcohol. Unfortunately, my stock of material being nearly exhausted, I could not examine this product any further.

#### *Dyslyte.*

The less soluble crystalline body separates from boiling alcohol, in which it is difficultly soluble, in fine long needles. Its purification is comparatively easy, owing to its insolubility. Its melting point is constantly 189° (corrected). On cooling, it solidifies suddenly, but at temperatures varying between 135° and 165°.

On analysis it gave the following results:—

I. 4218 grm. gave 586 carbonic acid and 096 water.  
 II. 4053     "     5605     "     "     0905     "  
 III. 2473     "     43.26 cc. nitrogen, at 0° and 760 mm., corresponding to the percentages—

	I.	II.	III.
Carbon .....	37.89	37.71	—
Hydrogen .....	2.53	2.48	—
Nitrogen .....	—	—	21.97

leading to the formula,  $C_8H_6N_4O_6$ , which requires—

	Theory.	Exp. (mean.)
Carbon .....	37.80	37.80
Hydrogen .....	2.36	2.50
Nitrogen .....	22.05	21.97

This substance is also decomposed by alcoholic potash, with formation of brown resinous products.

The fluid product accompanying the two solid substances was precipitated by water from the last mother-liquors of the crude product, and purified as far as possible by distillation in a current of steam (a small quantity of the solid products coming over also), and the distillate shaken up with ether. On evaporation of the clear ethereal solution, a small quantity of a yellow oil remained, having the characteristic smell of volatile nitro-compounds. On the application of a strong heat it exploded violently.

On reduction it gave apparently nothing but ammonia, and some tarry matter.

I regret very much that the very small yield of the products in question, together with the difficulties in their purification, have prevented me at present from further investigation; but I have commenced the preparation of a further quantity, which will enable me to examine more particularly the basic derivatives, from which I anticipate interesting results, which I hope to communicate on a future occasion.

## VI.—On Quinicine and Cinchonine and their Salts.

By DAVID HOWARD.

IN the early part of last year I brought before the notice of this Society an account of an alkaloid from cinchona bark, the properties of which distinguished it from those already described.

Further investigations, following out a suggestion which I owe to

Dr. de Vrij, of the Hague, convince me that it is identical with the quinicine, first obtained by Pasteur from quinine by the action of heat, and described by him in a paper, a translation of which is to be found in the Journal of the Chemical Society, vol. vi, p. 274.

I now supplement the brief account there given by a more particular description of the crystalline salts of this singular alkaloid, and of the similarly formed cinchonine, the allusions to which are very slight in Pasteur's paper; and believe that the result of a further examination will be found to add something to our knowledge of the history of the cinchona alkaloids, and to throw some light on the vexed question of the identity of quinicine with the uncrystallised alkaloids contained in these barks, which in an impure state form the quinoidine of commerce, which Pasteur suggests in the above-mentioned paper, but which still remains undecided.

The result of many experiments on the transformation of quinine and quinidine into quinicine; and of cinchonine and cinchonidine into cinchonicine, confirm Pasteur's observations that, "though heat plays an important part in this transformation, the vitreous resinoidal state of the product has nevertheless a real influence on it." Thus we find that the action of heat on a solution of a salt of an alkaloid in water in sealed tubes, even when exposed to a higher temperature than is required under favourable circumstances to convert it wholly into the isomeric modification, is very slight indeed; if, however, a considerable excess of acid be present, the alkaloid is, under the same circumstances, slowly changed, but far less readily than when Pasteur's conditions are observed. On the other hand, acting on a hint of Dr. de Vrij's, I find that a mixture of glycerin and neutral sulphate of cinchonine, exposed to the needful heat, is converted into sulphate of cinchonicine *pari passu* with a mixture of the salt with acid. Sulphate of quinine when heated with glycerin, showed no signs of the formation of quinicine, owing apparently to the slight solubility of the salt in that medium.

The change in the alkaloids is accompanied in all cases by the development of a yellow colour, which seems inherent in the resulting alkaloid; if more heat is used than is absolutely needed, especially when atmospheric air is present, a further decomposition takes place with formation of a darker colour; this may be in great part prevented by heating in an atmosphere of carbonic anhydride.

A careful examination of the salts of quinicine shows that the alkaloid described in my previous paper is identical with it. The greater number of these salts are difficult to crystallise, but the chloroplatinate, the oxalate, and the acid tartrate crystallise with comparative ease, and can be obtained in a state of purity. We are thus enabled to observe a fact of some importance, that the salts of quinicine pre-



pared from quinine are exactly similar in all their properties to those prepared from quinidine; in fact, that there is but one quinicine, from whichever of the isomeric bases it may have been derived.

The chloroplatinate precipitated from a hot solution forms a crystalline powder; it can be obtained in definite crystals from a hot acid solution. Its formula is  $C_{20}H_{24}N_2O_2 \cdot 2HCl.PtCl_4$ . Analysis gives the following results:—

	Pt.
Chloroplatinate of alkaloid prepared from quinine ..	26·58 p. c.
"          "          "          "          " ..	26·42
"          "          "          "          quinidine..	26·45
"          "          "          "          extracted from quinoïdine	26·63
Theory requires .....	26·76

The oxalate, as previously described, has the formula,  $2C_{20}H_{24}N_2O_2 \cdot C_2H_2O_4 + 9H_2O$ . The analysis gives results as under—

	$C_2H_2O_4$ .	$H_2O$ , 7 at. lost <i>in vacuo</i> .	$H_2O$ , 9 at. lost at 100 c.
Theory .....	10·00	14·00	18·00
Average of previous determinations of oxalate from quinoïdine .....	10·11	14·04	17·91
Oxalate of quinicine prepared from quinine .....	9·99	14·37	18·02
Oxalate of quinicine prepared from quinidine .....	—	13·90	18·05
Oxalate of quinicine prepared from quinidine .....	9·96	14·08	17·83
Oxalate of quinicine prepared from quinidine .....	—	14·00	17·83

The acid tartrate crystallises freely from strong solutions in radiated needles; the determinations of  $H_2O$  and  $C_4H_6O_6$  agree with the formula,  $C_{20}H_{24}N_2O_2 \cdot C_4H_6O_6 + 6H_2O$ . The salt fuses readily when exposed to a heat of  $100^\circ C$ . By gradual drying at about  $50^\circ$ , it loses 4 atoms of water; and by heating to  $140^\circ$ , the remaining 2 atoms are expelled, with fusion of the salt and slight discoloration. Analysis gives the following figures:—

	$C_4H_6O_6$ .	$H_2O$ , 4 at. lost at $50^\circ C$ .	$H_2O$ , 6 at. lost at $140^\circ C$ .
Theory .....	25·77	12·37	18·56
Acid tartrate of quinicine prepared } I. from quinine .....	26·05	12·80	19·36
} II. 	25·29	13·00	—
Acid tartrate of quinicine prepared } I. from quinidine .....	25·26	11·97	19·31
} II. 	25·23	11·83	18·88
Acid tartrate of quinicine prepared } I. from quinoïdine .....	25·97	13·55	17·99
} II. 	25·66	13·00	19·29

*Cinchonicine* and its salts are very similar in their properties to quinicine and its salts; the alkaloid is soluble in ether, separating

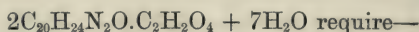
like quinine, as an oily layer at the bottom of the solution as the ether evaporates. The salts are somewhat more soluble than the corresponding quinine salts. The same identity is observed between those prepared from cinchonine and those from cinchonidine that is found between the salts of quinine prepared from quinine and from quinidine.

The *platinochloride* gives the following results, showing the formula to be  $C_{20}H_{21}N_2O \cdot 2HCl \cdot PtCl_4$ :—

	Pt.
Theory .....	27·36
Platinochloride of cinchonicine prepared from } cinchonine .....	27·65 27·61
Platinochloride of cinchonicine prepared from } cinchonidine .....	27·52 27·63

The *oxalate* differs from the oxalate of quinine by containing only 7 atoms of water; it very readily loses a portion of this water, and is therefore difficult to dry for analysis; the whole is given off at  $100^\circ C$ . No definite point of hydration is reached by drying *in vacuo*. It is somewhat more soluble than the quinine salt.

Analysis gives the following results:—



	$C_2H_2O_4$ 10·82.	$7H_2O$ 15·14.
Oxalate of cinchonicine prepared from } cinchonine gives .....	11·06 10·90 11·07	14·30 15·18 —
Oxalate of cinchonicine prepared from } cinchonidine.....	11·00 11·05	14·76 15·55

The *acid tartrate* crystallises in crusts composed of short prisms; this salt contains but one atom of water, which it loses at  $120^\circ C$ . without fusion.

The formula,  $C_{20}H_{24}N_2O \cdot C_4H_6O_6 + H_2O$  requires—

	$C_4H_6O_6$ 31·51.	$H_2O$ 3·70.
Acid tartrate of cinchonicine prepared from } cinchonine gives .....	32·49 31·33	3·83 3·80
Acid tartrate of cinchonicine prepared from } cinchonidine.....	32·27	3·68

The action of these alkaloids on polarised light also shows the

identity of the resulting alkaloid produced by the action of heat on the isomeric alkaloids, the different action on the polarised ray disappearing with the other characteristic distinctions. Quinicine, either from the strongly levogyrate quinine, or from the dextrogyrate quinidine, exhibits a comparatively feeble right-handed rotation, identical within the limits of errors of observation.

The observed molecular rotatory powers of these alkaloids for the yellow ray are as follows:—

In a spiritous solution of the alkaloid—

Quinicine from quinine	.... $\nearrow 39^\circ$
Quinicine from quinidine	.... $\nearrow 39^\circ$
Quinicine from quinoïdine	.... $\nearrow 39.3^\circ$

Oxalate of quinicine in an acid solution—

Prepared from quinine	.... $\nearrow 13.4^\circ$
Prepared from quinidine	.... $\nearrow 14^\circ$
Prepared from quinoïdine	.... $\nearrow 14^\circ$

Cinchonine in a spiritous solution—

Prepared from cinchonine	.... $\nearrow 48^\circ$
Prepared from cinchonidine	.. $\nearrow 48.4^\circ$

Oxalate of cinchonine in an acid solution—

From cinchonine	..... $\nearrow 18^\circ$
From cinchonidine	..... $\nearrow 17.9^\circ$

It will be observed that the rotatory power in both cases is much less in an acid solution than in a spiritous solution of the alkaloid.

It is very difficult to determine what is the exact nature of the change we have been considering. The examination of the optical and chemical properties of successive crystallisations of these salts fails to detect signs of the existence of more than one homogeneous product. The high colour of some of the later crystallisations prevented the use of solutions in the polarimeter strong enough to give more than a very small angle of rotation, and perfectly accordant results are thus unattainable. Still the differences observed between the first and the last crystallisations from considerable quantities are too small to throw doubt on their identity.

Thus the molecular rotation observed in the oxalate of quinicine from the mother-liquor of salts of the alkaloid prepared from quinine was  $\nearrow 13.3^\circ$ , and of the alkaloid in solution in spirit  $\nearrow 31.6^\circ$ ; that of similarly prepared oxalate from quinidine  $\nearrow 12.2^\circ$ . Cinchonine from the last mother-liquors prepared from cinchonine showed a rotatory power of  $\nearrow 44.5^\circ$ , and its oxalate  $\nearrow 18.5^\circ$ , while the last portions prepared from cinchonidine showed  $\nearrow 40^\circ$ .



The question now arises: is the uncrystallisable alkaloid obtained from chinchona bark quinine, or is it yet another alkaloid really uncrystallisable. Hitherto the most careful purification has failed to obtain crystalline salts from it such as have been described. When quinine is present, it will, as has been stated, crystallise out of the mixture, but the bulk of the quinoïdine, however carefully purified, refuses to crystallise even after many months' standing. It seems highly improbable, though of course it is possible, that this is owing to some impurity which hinders the crystallisation: for we find that quinine-salts prepared from crystallisable alkaloid crystallise entirely with comparative freedom, even when the heat used in its formation has been considerably above the point needed, and sufficient to decompose a portion, and there is no sign of any amorphous modification being formed.

Quinoïdine closely resembles quinine in other respects. When purified, as far as possible, by fractional precipitation and solution in ether, it forms a readily fusible yellow resin. The platinochloride precipitates as an amorphous powder, readily fusible, slightly soluble in hot water, and much more so in hot dilute hydrochloric acid, from its solution in which it falls out on cooling, as an amorphous powder, which under the microscope appears to consist of globules without any sign of crystallisation.

The salt precipitated from a cold solution contains 26.59 per cent. of platinum, and after solution in dilute acid 26.28 per cent.; it is, therefore, isomeric with quinine and quinine.

It is difficult to speak with certainty of the optical properties of this alkaloid, on account of the great difficulty of insuring absolute purity from the other alkaloids of higher rotatory power, a very small percentage of which would evidently vitiate the results. The specimen, the analysis of the platinum salt of which is given above, showed a specific rotatory power of  $+33^{\circ}$ ; other specimens gave higher results, but their purity was more doubtful.

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# ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

## Physical Chemistry.

### Thermochemical Researches on the Formation of Precipitates.

By M. BERTHELOT. (Compt. rend. lxxiii, 1105—1113; 1162—1165, and 1215—1219).

In general, when a precipitate is formed, there is a disengagement of heat, the same as in the solidification of a melted substance; but in the former case the operation is much more complicated, as various other actions have to be considered, such as crystallisation, change of aggregation, &c.

1. *Formation of a Solid Compound.*—The heat disengaged in the formation of a precipitate is due in great part to the separation of a solid body, as is shown by an examination of those salts which produce precipitates only when the solutions are concentrated, such as lead, chloride, potassium picrate, and calcium tartrate. *Lead Chloride.*—On adding a dilute solution of sodium chloride to one of lead nitrate, so that no precipitate is formed, an absorption of heat takes place, about equal to that produced by the dilution of the lead solution; but when a precipitate is formed, there is a disengagement of + 2.0 heat-units for each equivalent of lead chloride ( $\text{PbCl}$ ) actually precipitated. *Potassium Picrate.*—If dilute solutions of potash and picric acid be mixed, the heat disengaged corresponds to that of neutralisation, but when a precipitate is obtained, + 10.0 heat-units are disengaged for each equivalent of salt precipitated. *Calcium Tartrate.*—Solutions of sodium tartrate and calcium chloride remain limpid when first mixed, heat being at the same time disengaged (+ 1.04). After the lapse of some minutes, however, a crystalline precipitate of calcium tartrate is formed, accompanied by a farther disengagement of heat (+ 2.96). From each of these examples it may be seen that it is not the chemical reaction which causes the chief disengagement of heat; but it must not be imagined that all precipitation is attended with evolution of heat, as the effects of dehydration, &c., sometimes render it even negative.

2. *Dehydration of the Compounds Precipitated.*—*Lime.*—Andrews has observed that the precipitation of lime from dilute solutions by potash gives rise to an absorption of heat, which may be explained by the fact that calcium hydrate dissolves in water with disengagement of heat, so that the precipitation of lime should be accompanied by a dehydration, that is a decomposition, the heat absorbed by which more than compensates for that which is disengaged during the solidification of the calcium hydrate. *Calcium carbonate* also, precipitated in the amorphous state, gives rise to an absorption of heat, which the author believes to be due to the partial dehydration of the compound at the moment of its precipitation. *Magnesium carbonate, ferrous carbonate,*

and *manganese carbonate*, give rise to an absorption of heat, representing a dehydration of the insoluble compound.—*Calcium sulphate* and *strontium sulphate*. The mixed solutions of sodium sulphate and calcium or strontium chloride remain clear, a slight absorption of heat taking place; on causing precipitation, however, by the introduction of some crystals of the sulphate, there is a slight disengagement of heat.—*Barium sulphate*, when precipitated, on the contrary, evolves considerable heat (+ 2.5 to + 2.9). These results indicate the existence of a thermic action of a contrary sign to that of solidification, and varying in the different salts.

3. *Separation of the Acid and Base in Salts*.—Not only can the saline hydrates which exist in solution be transformed into precipitated hydrates of a different type by double decomposition, but even a partial or total separation between the acid and base may be effected, in which case, as in that of dehydration, heat is absorbed. In general this decomposition is not complete, the normal compound being separated into two others, a basic hydrated salt, which is precipitated, and an acid salt which remains dissolved.—*Zinc Carbonate*. Its composition varies according to the temperature and the proportions of water, base, and carbonic acid which are present, an absorption of heat taking place. In the normal reaction, when equivalent quantities are used, the total absorption of heat does not take place at once, a secondary reaction setting in by which a farther but comparatively small amount is absorbed. These phenomena correspond to the formation of a basic hydrocarbonate mixed with double salts of variable composition. If an alkaline bicarbonate be substituted for the carbonate, neutral zinc carbonate is precipitated, the heat absorbed in this case being much less than with the alkaline carbonates. This reaction also takes place in two stages, and after a time a third action commences, accompanied by an absorption of heat, and a very feeble evolution of gas. This is due to the formation of zinc bicarbonate, which subsequently undergoes decomposition, neutral zinc carbonate (mixed with a double salt) being precipitated, and carbonic acid remaining in solution. The absorption of heat is more feeble than with the neutral alkaline carbonates, as it represents only the decomposition of the zinc bicarbonate into neutral carbonate and carbonic acid.—*Copper carbonate*, precipitated by an alkaline carbonate, produces in strong solutions (1 equiv. = 2 lit.) an absorption of heat, which, like the precipitation, is immediate; after a short time effervescence sets in with further cooling, indicating that normal cupric carbonate has but an ephemeral existence.—*Ferric carbonates*. On treating crystalline ferric nitrate with potash, 7.87 heat-units were disengaged, from which the author calculates that ferric nitrate (1 equiv. = 2 lit.) poured into potassium carbonate (1 equiv. = 2 lit.) would absorb - 0.10. He has also examined ferric sulphate and iron-alum, and concludes from the results that no definite ferric carbonate is formed, but divers complex systems containing a basic salt, an acid salt, and free acid.—*Alumina*. From the results of treating aluminium sulphate with potassium carbonate, it would appear that a molecular condensation of the alumina takes place.—*Chromium*. With chrome alum and an alkaline carbonate there was, at first, an absorption of heat, and



afterwards a feeble effervescence, accompanied by a disengagement of heat, from which the author infers that there is a special molecular change in the chromium oxide comparable to the formation of a polymeric body.

4. *Changes in the State of Aggregation.*—This is the case of those precipitates which in the first instance are amorphous, but gradually aggregate and finally become crystalline; these successive changes, which may be observed under a microscope, give rise to an evolution of heat. *Strontium carbonate* is precipitated in an amorphous state, accompanied by absorption of heat ( $-0.40$ ), but the precipitate after a time becomes crystalline, causing an evolution of heat  $+0.40$  to  $+0.56$ . With *barium carbonate* the difference between the two actions is less marked. *Lead carbonate* at first disengages  $+0.40$ , but the thermometer mounts rapidly, and ultimately the amount of heat disengaged is  $2.52$ . In *silver carbonate* the thermic results correspond to amorphous states which succeed one another too rapidly to be distinguished. From results obtained with dilute solutions however, the author has calculated that the heat evolved in the combination of carbonic acid and hydrated silver oxide, exceeds that of the formation of silver nitrate. The precipitation of the *ovalates*, which are for the most part crystalline, disengages much heat, the calcium salt evolving as much as barium sulphate.

Many effects marked by thermic phenomena are produced during the double decomposition of salts; at the moment when the solutions are mixed, a certain definite equilibrium is attained depending upon the proportions of water, of the primitive salts, and of those newly formed; but when these latter are insoluble, they undergo further changes both chemical and physical, such as dehydration, crystallisation, &c. The heat disengaged therefore is not the measure of the forces set in action, except in those cases where each individual change causes an evolution of heat, or the contrary.

C. E. G.

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**On the most Economical Arrangement of Voltaic Batteries with respect to their Polar Electrodes.** By T. du MONCEL (Compt. rend., lxxiii, 1166—1168).

THE author's former conclusions (pp. 88, 1182 of last volume) apply only to piles which are susceptible of being polarised, and whose electrodes are immersed in the same homogeneous liquid. That the most prejudicial effect of the reduction of a polar electrode corresponds to that one of the two electrodes which is immersed in the liquid possessed of the least conductivity, was shown by the results obtained with a Daniell's battery excited with a dilute solution of zinc sulphate in one experiment, and in another with water acidulated with sulphuric acid. Analogous effects are observed in the currents arising from the oxidation of metallic plates buried in the earth, the direction of the current being reversed by watering the soil around one of the plates (*Annals of Telegraphy*, iv, 472).

When the exciting liquids are equally good conductors, as in a Daniell's battery, in which the solution has become saturated with zinc

sulphate, the battery polarises but little, and therefore the effects are not very marked, although distinctly recognisable. When there is antagonism between the polarities of the chemical elements in contact with a metallic plate, the effects take place more quickly and completely in plates of small surface than with larger ones, from which it would seem that *the reactions may vary according as the effects of polarisation are more or less in excess of the effects of conductivity*. This the author shows to be the case from the results obtained with a Daniell's battery charged alternately with cold and with boiling water.

C. E. G.

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**Thermic Researches on the Electrolysis of the Alkaline Bases and Sulphates.** By P. A. FAVRE (Compt. rend., lxxiii, 1036—1040).

In this paper the author describes experiments tending to confirm his former conclusion (p. 987 of the last volume of this Journal) that a battery composed of five pairs of Smee's elements effects the decomposition of the alkalis and their salts only by virtue of the addition of energy which it derives from the oxidation of the metal itself, this oxidation constituting a "synelectrolytic" phenomenon, that is to say, taking place simultaneously with the electrolysis.

Three series of experiments were made in such a manner as to prevent the direct decomposition of the water by the greater part of the metal.

The battery of five pairs of Smee's elements (the voltaic energy of which was equivalent to 75,000 heat-units: see pp. 985, 1134 of last volume) was placed within the mercury-calorimeter as before, together with a thermorheostat; but as this battery was unable to effect the electrolysis of the alkaline salt when the separated metal was prevented (by the use of a two-celled voltameter) from combining synelectrolytically with the oxygen of the decomposed water, it was reinforced by a number of exactly similar auxiliary pairs placed outside the calorimeter; and in the first series of experiments, the power of the thermorheostat within the calorimeter was increased so far as to render the physical resistance of these couples inappreciable. In the second series of experiments, two thermorheostats were used, one within the calorimeter, the other without, their united resistances being equal to that of the single rheostat previously employed, and the resistance of each being proportional to the number of interior and exterior voltaic couples corresponding to them. In the third series of experiments, the thermorheostat was omitted.

The quantity of heat which would have been absorbed and exhibited by the calorimeter if all the voltaic couples had been enclosed therein, is represented by the number of heat-units actually absorbed by the calorimeter for one equivalent of zinc dissolved, increased, in the first series of experiments, by  $4,500 \text{ heat-units} \times \frac{c}{C}$ ; in the second by

$\frac{A}{5} \times c$ ; and in the third by  $5 \frac{A}{5} \times c$ , together with the calculated

quantity of heat borrowed from the battery to overcome the resistance of the voltameter.

In these formulæ,  $C$  denotes the total number of couples employed;  $c$  the number outside the calorimeter;  $A$  the number of heat-units absorbed and manifested by the calorimeter for each equivalent of zinc dissolved in the couples.

To avoid the synelectrolytic decomposition of the water by the greater part of the metal set free by the electrolysis, the aqueous solution of the salt or alkali was introduced into the exterior compartment of the divided voltameter, and the interior porous vessel, after being saturated with the same solution, was filled with mercury. This solution was thus in contact with the mercury, in which was immersed one of the conducting wires, terminated by a thick wire of platinum, while the other conductor, terminated by a broad platinum plate completely surrounding the porous vessel and constituting the positive electrode, was plunged into the external compartment.

By this arrangement, the alkali-metal set free at the negative electrode was enabled to amalgamate with the mercury. When, however, only five couples were used, this amalgamation was impossible, because as already observed, the electrolysis itself did not take place; but when the voltaic energy of the battery was increased by a sufficient number of additional pairs, the quantity of heat borrowed by the voltameter and expended in the electrolysis was much greater, and the mercury of the negative electrode became charged with a considerable proportion of alkali-metal. In the electrolysis of ammonia and its sulphate, the volume of the mercury was considerably augmented. The alkali-metal thus fixed by the mercury became gradually oxidised by decomposing the water in contact with it; but this oxidation, taking place after the electrolysis (and being therefore a *meta-electrolytic phenomenon*) did not further strengthen the voltaic energy of the battery.

It must be observed, however, that a certain quantity of the alkali-metal which is separated escapes amalgamation, and is directly oxidised by contact with the water, inasmuch as the quantity of heat borrowed by the voltameter to electrolyse the alkalis and their salts is always less than it would be if the separated metal had been completely preserved from contact with the water.

From the experiments described in this and his preceding communication, the author concludes that the oxides and salts of the alkali-metals, when subjected to the action of the electric current, are decomposed and give up their metal, which metal being *directly oxidised* at the expense of the oxygen of the water, sets free a certain quantity of heat which reinforces the voltaic energy of the battery.

H. W.

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**Thermic Researches on Electrolysis** (*continued*). By P. A. FAVRE (Compt. rend., lxxiii, 1085—1090; 1186—1191; and 1258—1262).

In these new series of experiments, the same method was employed as in the research on the electrolysis of the oxides and sulphates of the



alkalis (p. 985 of last volume), and the same mode of calculation as in the last paper (p. 110 of this volume).

These experiments strengthen the conclusions arrived at before, that the heat borrowed from the battery for the electrolysis of sulphuric acid and nitric acid, cannot be considered as the true thermic expression of the heat of formation of these acids.

Further, it appears from these experiments, that the secondary reactions which accompany the electrolysis and produce heat not transmissible to the circuit, always tend to strengthen the energy of the battery whenever the current is weak, and when the electrolysis offers great resistance. Such secondary reactions are, for example, produced by the hydrogen and the oxygen set free during the electrolysis, the first being burned, the second oxidising any oxidisable substance present; also by the decomposition of certain radicals set free, which, like the metalloïd radical of oxalic acid, are explosive.

On the other hand, the more the energy of the battery is increased by using a greater number of cells, the less does it appear to be favoured by the secondary reactions in the voltameter. It is therefore very difficult to determine exactly the quantity of heat which is due to the battery, and transmissible or not transmissible to the circuit.

The author discusses the results obtained for oxalic acid  $\text{HC}_2\text{O}_4^*$  for the electrolysis of which 38,635 heat-units are borrowed from the battery, whilst 31,471 remain within the voltameter. Now he had shown on a former occasion, that the decomposition of oxalic acid into carbonic acid and water disengaged 30,140 heat-units, and that 131,422 are evolved by the complete combustion of two equivalents of carbon and one equivalent of hydrogen. The difference 101,282 expresses the total heat evolved during the formation of oxalic acid from its elements.

But the electrolysis of oxalic acid into  $\text{C}_2\text{O}_4$  and  $\text{H}$  requires 38,635 heat-units, which, subtracted from 101,282 leave 62,647 as the heat of formation of the radical  $\text{C}_2\text{O}_4$ ; now as 96,960 heat-units are set free during the formation of two equivalents of carbonic acid, it follows that  $96,960 - 62,647 = 34,313$  expresses the number of heat-units liberated during the splitting up of the radical  $\text{C}_2\text{O}_4$  into  $2\text{CO}_2$ . This, therefore, ought to be the number of heat-units evolved in the voltameter, instead of 31,471 units which are actually obtained. This difference may, however, be ascribed to the unavoidable errors of experiment.

The following are the quantities of heat borrowed from the battery in the electrolysis of certain zinc and copper salts:—

Salts.	Heat borrowed from the battery.
Zinc sulphate . . . . .	65510 units.
Copper sulphate . . . . .	39415 „
Copper acetate . . . . .	37770 „

A detailed account is given of the influence of the sulphuric acid

\*  $\text{C} = 6$ ;  $\text{O} = 8$ .

formed during the electrolysis upon the progress of the decomposition.

A great part of the sulphuric acid set free during the electrolysis of zinc sulphate is electrolysed instead of the zinc salt, because it offers less resistance to decomposition, and consequently less heat is withdrawn from the battery than would be required for the decomposition of the zinc salt. This electrolysis of the sulphuric acid instead of the metallic salt, is greatly augmented when the resistance is increased, as for instance, by inserting the thermorheostat. This disturbing influence of the sulphuric acid can be avoided by employing a large quantity of zinc solution, about 2 litres, in the voltameter, because then the sulphuric acid formed during the operation is immediately diluted to such an extent that its electrolysis, in comparison with that of the zinc salt, may be neglected.

When, on the other hand, cupric sulphate is electrolysed, which offers less resistance to its decomposition than sulphuric acid, the latter increases rapidly, and it becomes necessary to employ the thermorheostat—(1) in order to render the resistance of the voltameter small compared with the total resistance of the circuit; (2) to retard the electrolysis so far that the cupric sulphate may have time to approach the negative electrode in the same proportion in which it is decomposed, as otherwise the sulphuric acid would be electrolysed in the place of the copper-salt.

Numerical results are given supporting these views.

In electrolysing a mixture of the three sulphates of zinc, cadmium, and copper, the author has succeeded, by altering the condition of the experiments, in obtaining at will, one metal or two metals at the same time, or all the three metals in certain proportions. The results of the operations vary, 1st, with the voltaic energy of the battery; 2nd, with the electrolytic resistance of the salts employed; 3rd, with the relative quantity of each salt; 4th, with the more or less rapid progress of the operation, which can be regulated by means of a rheostat.

Since this behaviour is exhibited, not only by mixtures of salts with the same acid, but also by mixtures of salts containing different acids, the author concludes that by varying the conditions just mentioned, we are able to withdraw from a mixture of salts the different metallic radicals successively, and in fact *to perform an analysis by employing voltaic energy instead of the ordinary chemical reagents.\**

When the galvanic current passes through the solution of some metal between plates of the same metal, the salt is simultaneously decomposed and reproduced; but although the chemical effects appear to neutralise each other, there is some heat evolved within the voltameter. The author has determined the heat evolved when solution of cupric sulphate is electrolysed between copper plates.

A wooden trough was provided with 20 equidistant grooves for copper plates. As these could be put in or taken out at pleasure, the trough, which was filled with solution of cupric sulphate, could be divided into any number of voltameters less than 20.

\* A process which has been proposed before on various occasions.

The battery used, consisting of four Smee's elements, was placed, together with the thermorheostat, within the calorimeter, whilst the trough remained without. Of the numerical results contained in the original paper a few are given here to show the method employed.

Plates used.	Heat indicated by the calorimeter corresponding to 1 equivalent of H evolved in the battery.	Heat spent outside of the calorimeter.	Calculation.	Heat spent outside of the calorimeter during the simultaneous decomposition and reproduction of cupric sulphate.	Calculation.	Heat borrowed from the battery during the simultaneous decomposition and reproduction of 1 equivalent of cupric sulphate and remaining in the voltameter.
	Heat-units.	Heat-units.		Heat-units.		Heat-units.
1 and 2 . . . .	19156	334	$\times 4 =$	7376	$1376 - r =$	982
1 and 20 . . . .	17384	2116	$\times 4 =$	8464	$\left\{ \begin{array}{l} 8464 - 1376 = 7088 = s \\ 7088 - 18 = 394 = r \end{array} \right\}$	—
The trough is removed from the circuit ..	19500	—	—	—	—	—

$s$  denotes the resistance, expressed in heat-units, of the liquid between the plates 2 and 20, and  $r$  the resistance of the liquid between the plates 1 and 2.

The multiplication by 4 in the fourth column is necessary, because in the four cells of the battery there are 4 equivalents of hydrogen evolved for every equivalent of cupric sulphate acted upon in the voltameter.

Next a combination of five voltameters was placed within the calorimeter, and one Smee's cell, together with the thermorheostat without. The plates of the voltameters were of the same size and the same material (rolled copper) as those of the first set of experiments, and the cupric sulphate of the same strength as before. After the current had passed for some time, and a deposit of copper had formed on the plates, the poles were reversed, so that now deposited copper had to be dissolved instead of rolled copper.

The author found that the change of poles produced no noticeable difference in the results, and obtained from the first set of experiments, as well as from the second, about 1,000 heat-units as the heat evolved during the electrolysis of one equivalent of cupric sulphate between copper plates.

The author infers from his experiments that—1. A certain quantity of the voltaic energy borrowed from the battery for the decomposition of a salt which is immediately reproduced, is converted into heat, and remains in the voltameter as heat, which is not transmissible to the circuit. 2. This conversion of voltaic energy probably takes place



whilst the metal passes from the state in which it is present in the saline solution into its elementary state, resuming its metallic properties. On the other hand, the copper of the plates, in order to pass from its truly metallic state into that modification in which it is present in its solutions, consumes heat derived from the battery.

If from the 10,500 heat-units evolved during the electrolysis of cupric sulphate between platinum plates we subtract 1,000 units due to the separation of copper, we obtain 9,500 units as the thermic expression of the change of state which the oxygen undergoes during its liberation.

The analogous expression for the liberation of one equivalent of hydrogen is 4,000 heat-units, obtained by subtracting 9,500 from the 13,500 units evolved during the electrolysis of one equivalent of hydrogen sulphate between platinum plates.

R. S.

**Researches on the Thermic Co-efficients of Hydroelectric and Thermoelectric Currents.** By F. M. RAOULT (Compt. rend. lxxiii, 949—951).

WITH regard to Joule's formula  $V = KeF$ , in which  $V$  denotes the total heat generated in the whole circuit during the passage of the unit of electricity, and  $F$  the electromotive force, it had been shown by former experiments that the co-efficient  $Ke$  is independent of the number of cells used; the author has, by two series of experiments, proved that it is also independent of the nature of the battery.

1. Two currents of equal strength, but produced by batteries of different nature, were successively made to pass through one and the same platinum wire, and the heat given off by each during the same time was measured and found (within 1 per cent.) to be equal, whether the battery used was that of Daniell or of Bunsen, or of the thermoelectric pile of Mure and Clamond. This method did not allow of more accurate determinations.

2. Two currents, passing through a differential galvanometer, were kept at equal strength by a rheostat of cupric sulphate, which was interposed in one of the circuits; each current passed through one of two platinum wires of equal resistance, placed within a thermorheometer, which most exactly indicated the heat given off by the wire.

The quantities of heat produced by currents of equal strength were found to be equal within  $\frac{1}{4}$  of 1 per cent., whether the current was derived—1. from Mure and Clamond's thermoelectric pile of 62 elements; 2. from a battery of 5 of Bunsen's elements; 3. From a battery of five Daniell's elements. Hence: (1) *the heat generated by an electric current is independent of the nature of the battery*; (2) *The co-efficient  $Ke$  is the same from whatever source the electric current may be derived.*

R. S.

**On the Influence of certain Liquids in Retarding or Arresting the Action of Acids upon Metals.** By C. MARANGONI and P. STEFANELLI (*Il nuovo Cimento* [2], iv, 373—389).

THE evolution of hydrogen from dilute sulphuric acid by the action of zinc, is quickly arrested on adding a small quantity of an essential oil, such as oil of myrtle, thyme, lavender, turpentine, or cherry-laurel, and agitating briskly with a glass rod, but recommences, though less strongly, on addition of a certain quantity of alcohol. Fixed oils likewise arrest the action completely, but less quickly than essential oils; ether, naphtha, benzene, and nitrobenzene have but little effect, the evolution of hydrogen being merely retarded by them while the agitation continues, and recommencing soon after the liquid is left at rest. The action of dilute nitric acid on copper is retarded by essential oils while they are agitated with the liquid, but quickly recommences on repose; fixed oils produce but little retardation; ether, naphtha, benzene, and nitrobenzene scarcely any. Similar remarks apply to the effect of these various liquids on the action of hydrochloric acid upon zinc. That of dilute nitric acid on zinc is not sensibly retarded by either of them.

The retarding action in all these cases is due to the formation, on the surface of the zinc, of a film of liquid which protects the metal from contact with the acid. The agitation of the mixture facilitates the formation of this film, partly by bringing the particles of the oily liquid in contact with the metal, partly by removing the bubbles of hydrogen which adhere to its surface.

Comparing their own observations with those of Duclaux (*Ann. Chim. Phys.* [4], xxi, 378) on the surface-tension of liquids, the authors conclude that the permanence of the protecting film is greater in proportion as the density of the oily liquid approaches more nearly to that of the acidulated water, and diminishes in proportion as this liquid has a greater superficial capillary tension (which is proportional to the product of its density into the height to which it rises in a capillary tube of given diameter). The fixed oils produce but little retarding effect, because, though they differ but little from the acidulated water in density, they have a considerable superficial tension; ether, naphtha, and benzene, on the other hand, though their superficial tension is small, cannot form permanent films on the metal under the acidulated water, on account of their small specific gravity; but the volatile oils above mentioned have but little superficial tension, and a density (0.869—0.886) not differing greatly from that of the acidulated water: hence they have the greatest tendency to form permanent films on the surface of the zinc.

The authors also found that the effect of a film of essential oil on the zinc plates of a voltaic pile, is similar to that of amalgamation, preventing local action to a certain extent. It diminishes the quantity and intensity of the current at the commencement of the action, but renders it for a certain time more constant. After two or three hours, however, it stops the action altogether.

H. W.

**On some Points in Spectrum Analysis and on the Constitution of Induction Sparks.** By LECOQ DE BOISBAUDRAN (Compt. rend., lxxiii, 943—946).

THE increase of temperature of any source of light (flame or electric spark) is always accompanied by an increase of the *relative* brightness of the more refrangible rays, whilst the intensity of the less refrangible rays is weakened, sometimes to complete extinction. The salts of lithium evaporated in the flame of a Bunsen's burner, produce a very bright red and a feeble orange-red line; when, however, the flame is rendered hotter by a bellows, the orange-red line, although still remaining less intense than the red line, gains considerably in brightness, and besides, some blue lines become visible.

When, however, the induction-spark is made to pass close to the surface of a lithium solution, so as to evaporate it, the orange-red ray even surpasses the red one, and the blue lines become very clear.

Stannic chloride volatilised by the ordinary spark produces three green lines; 503·1, 588·9, 566·1, of which the first only is bright. When, however, the spark of a Leyden jar is used, the first line is weakened almost to extinction, whilst the others become bright.

In the lithium spectrum produced by the induction spark, the orange-red line is very feeble in the spectrum of the positive, but very intense in that of the negative pole.

If the difference of the spectra be due to the difference of temperature of the two electrodes, it must be possible to render them equal by raising the positive electrode to the same temperature as the other. By applying the blowpipe flame to the positive pole, the author succeeded only so far as to increase the relative brightness of the orange-red line of the lithium, and of the blue and violet lines of the sodium spectrum.

When, however, the electrodes of a middle-sized Ruhmkorff (30 centimeters long), excited by five bichromate couples (zinc 15 c × 10 c) were gradually approached to each other, the little blue spots characterising the negative pole were observed at the positive pole; the spectrum of the negative pole was then at intervals exhibited by the positive pole, till at last, at a certain distance of the poles, their spectra could no longer be distinguished from each other.

When the poles were approached to a distance of only  $\frac{1}{4}$  to  $\frac{1}{10}$  of 1 millimeter, the original state of things was reversed, inasmuch as the positive pole became brighter than the negative. Blowing upon the electrodes, reduced the temperature of the originally negative one, whilst the other one remained still red, and when the blowing became strong, both poles covered themselves with little blue spots.

The reversion of the conditions of temperature at the two poles, is facilitated by a great rapidity of the oscillations of the hammer.

An interruption of the induced current, however short, is followed by the restitution of the original conditions with regard to polarity, &c.

The author recommends the use of short induction sparks passing from a platinum wire for volatilising the substance whose spectrum is to be examined.

R. S.



**Shifting of the Spectrum Lines by the Action of Temperature on the Prisms.** By BLASERNA (Pogg. Ann. cxliii, 655).

It is frequently considered that the small range of temperature to which the prisms of spectroscopes are exposed is of no importance as regards their dispersive power. The author experimented with a flint glass prism by Duboscq, and found that the dispersion increased with decrease of temperature. In the spectroscope used by the author, the distance from D to D' was 12''; a change in the temperature of the flint glass prism, of 4° C., gave also an alteration of 12'' in the dispersion, and would therefore change the position of D to D'.

A. P.

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**Coloured Gelatin-films as Objects for the Spectroscope.**

By E. LOMMEL (Pogg. Ann. cxliii, 656).

THE author proposes the use of gelatin coloured with such substances as the aniline colours, chlorophyll, &c., for producing absorption spectra in the spectroscope. Colours soluble in alcohol and insoluble in water, give homogeneous and transparent films.

The chlorophyll-gelatin, however, does not give the absorption spectrum of the alcoholic solution of chlorophyll, but that of solid chlorophyll, as shown in the leaves of plants by transmitted light.

A. P.

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**The Spectrum of Lightning.** By H. VOGEL (Pogg. Ann. cxliii, 653).

THE author took advantage of a very vivid thunderstorm to examine the spectrum of lightning. A large spectroscope was used, the width of the slit being so regulated that the sodium lines were just separated. The following measurements of bright lines were obtained:—

- |    |                         |                                      |
|----|-------------------------|--------------------------------------|
| 1. | 534.1 millionths of mm. | —faint line.                         |
| 2. | 518.4                   | „ somewhat bright line.              |
| 3. | 500.2                   | „ very bright line, before a darker. |
| 4. | 486.0                   | „ bright line.                       |
| 5. | From                    |                                      |
|    | 467.3 to                |                                      |
|    | 458.3                   | „ broad bright band.                 |

There was another bright band near G, and some lines in the red, too faint to measure. Line 1 is found in the oxygen spectrum; 2, 3, and 5 are identical with lines in the air spectrum, and 4 corresponds with H  $\beta$ .

Some of the flashes gave only bright lines, others bright lines on a continuous spectrum, whilst others gave only a continuous spectrum.

A. P.

**Spectrum of the Aurora Borealis.** By G. F. BARKER  
(*American Journal of Science* [3] ii, 465).

THE spectrum of a very brilliant crimson aurora observed at New-haven, exhibited five well-marked lines, the positions of which on a millimeter scale, whose 100th division coincided with the sodium line, were 90, 110.5, 130, 138, and 149. Their brightness, following the above order, was 3, 1, 5, 2, 4. The fourth line, of wave-length 502, does not appear to have been previously observed in the auroral spectrum.

H. W.

**Phosphorescence produced by Increase of Temperature.** By  
A. FORSTER (*Pogg. Ann.* cxliii, 658—660).

WYROUBOFF, from his experiments on the phosphorescence of fluor spar by increase of temperature, has concluded that the phenomenon depends entirely on the organic matter contained in most samples of this mineral. Forster shows that, according to Wyruboff's analyses, the quantity of organic matter contained in strongly phosphorescent samples of fluor spar is less than that contained in specimens which are less fluorescent, and also that some samples of perfectly colourless fluor spar are strongly fluorescent when heated. A sample of fluor spar which has this property destroyed by strong heating, can be again rendered capable of becoming phosphorescent by exposure to electric sparks in a Leyden jar. These experiments completely refute Wyruboff's theory that the phosphorescence is due to the organic matter in fluor spar, as by the strong heating in the last case the organic matter must be destroyed.

A. P.

**The Colours of Metals.** By C. A. SEELY (*Chem. News*, xxiv, 223).

WHEN a coloured object is examined, the rays of light which meet the eye are always more or less diluted with white light, because the light which illuminates the surface of the object is never completely decomposed, a portion of it being always directly reflected. The colour of a polished metallic surface is ordinarily invisible, because the tint due to the feeble decomposition of the light is overpowered by the more powerful reflected ray.

The method heretofore adopted for rendering the colour of metals visible, consists in repeatedly reflecting a beam of white light from the metallic surface under examination. At each incidence the white light is partially decomposed, and if the number of incidences be sufficiently multiplied, the whole of the white light will disappear, and only the pure coloured rays be visible. The actual experiment, however, is not very successful, inasmuch as, by gradual dispersion, a large portion of the coloured rays is lost; the author, therefore,

proposes to modify the experiment by bringing into operation the well known law that "when white light is decomposed, the reflected coloured ray is complementary to the transmitted or absorbed ray."

For this purpose, a transparent solvent of the metals was required, which should have no chemical action upon them. In the case of the alkali metals, anhydrous liquid ammonia was found to answer successfully. When placed in this menstruum, these metals gradually dissolve, producing a solution which appears blue by transmitted light; from this circumstance it would appear that the natural colour of the alkali-metals by reflected light is copper-red.

Beyond this point the subject has not been successfully prosecuted; the author anticipates, however, that ere long the somewhat novel idea of the solution of metals without definite chemical action will receive a more careful investigation.

J. W.

*Report on Molecular Dissociation by Heat of Compounds in Solution.*

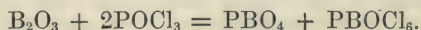
By C. R. C. TICHBORNE (Chem. News. xxiv, 199, 209, 220).

*Galvanic Battery Elements.* By W. H. COFFIN (Chem. News, xxiv, 231).

## Inorganic Chemistry.

**On the Mutual Substitution of some Metalloids.** By G. GUSTAVSON (Zeitschr. f. Chem. [2], vii, 417—418).

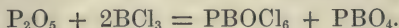
WHEN a mixture of boron trioxide and phosphorus oxychloride is heated in sealed tubes for 8 to 10 hours to 150°, the following reaction takes place:—



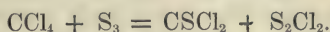
The compound  $\text{PBOCl}_6$  sublimes into the upper parts of the tubes, whilst  $\text{PBO}_4$  is left as a white mass, which dissolves completely in water, with formation of boric acid and phosphoric acid. From this it would appear that this body is either a mixture or a very loose compound. By ignition, however, it becomes insoluble in water, but dissolves in boiling alkalis, with formation of borates and phosphates. The crystalline compound  $\text{PBOCl}_6$  is also very readily formed by direct combination of boron trichloride and phosphorus oxychloride. On adding the latter substance to well cooled boron trichloride, a hissing noise is heard, and when the vapour of the trichloride is passed into the oxychloride, it is completely absorbed. The compound



$\text{PBOCl}_6$  is completely decomposed into its components by repeated sublimation, and slowly loses boron trichloride, even at the ordinary temperature. It is also instantaneously decomposed by water. In sealed tubes it melts at  $73^\circ$ . The same products are obtained by heating phosphorus pentoxide and boron trichloride for 2—3 days to  $200^\circ$ :



Sulphur and boron trichloride do not act on each other even at  $250^\circ$ ; but sulphur and carbon tetrachloride give readily at  $130^\circ$  the following reaction:—



C. S.

### On Stannic and Titanic Compounds crystallised from Fluxes.

By G. WUNDER (J. pr. Chem. [2], iv, 339—349).

1. *Stannic Compounds*.—As A. Knop (*Ann. Chem. Pharm.*, clvii, 363, and this Journal [2], ix, 200) had shown that the supposed anatase artificially prepared by Rose really contained phosphoric acid, the author determined to repeat his former experiments (*J. pr. Chem.* [2], ii, 206), and prepare larger quantities of the stannic compound, so as to be able to make analyses of it. The stannic compound, which crystallises from melted borax in tetragonal crystals of the same form as tinstone, was analysed and found to be stannic acid. The tetragonal pyramids isomorphous with anatase obtained from the solution of stannic acid in a fused mixture of borax and microcosmic salt, were found however to have the composition  $\text{SnNa}_2(\text{PO}_4)_2$ . Finally, the microscopic crystals which are obtained under similar circumstances from microcosmic salt, and might be mistaken for cubes were it not for their action on polarised light, have the formula  $\text{Sn}_2\text{Na}(\text{PO}_4)_3$ , and are sometimes accompanied by the tetragonal prisms just mentioned. A goniometric examination of larger crystals of this species showed that they were not really cubes, the angles differing from a right angle by somewhat more than  $2^\circ$ . The formation of the tetragonal prisms is facilitated when the stannic acid is relatively in large quantity, or when borax is present. This is owing to the formation of trisodic phosphate, as was proved by experiments made for that purpose, the rhombohedrons being converted into the tetragonal prisms, and *vice versa*, according as the flux contains less or more phosphoric acid:



Rhombohedra.

Tetragonal pyramids.

As Knop's paper on the same subject (p. 802 of last volume), appeared whilst these experiments were yet unpublished, assigning the formula  $2\text{SnO}_2 \cdot \text{P}_2\text{O}_5$  to the tetragonal pyramids, and to the rhombohedra the composition  $\text{SnO}_2 \cdot \text{P}_2\text{O}_5$ , the author again repeated them, with the same results, and attributes the discrepancy to Knop having

treated his crystals with fused phosphoric acid, whereby they were partly decomposed.

2. *Titanic Compounds*.—According to Rose (*Wien. Akad. Ber.*, 1867, 132) the crystals obtained by fusing titanic acid with microcosmic salt are quadratic tables, but Knop (p. 200 of last volume), finding that they were affected by polarized light considered them to be rhombic. The author, having prepared some large crystals of this compound measuring one mm. on the side, found, in fact, that they were acute rhombohedrons with angles of  $91^{\circ} 44'$  and  $88^{\circ} 16'$ . These crystals, to which Knop had assigned the formula  $3\text{TiO}_2 \cdot \text{P}_2\text{O}_5$ , were found by the author to possess the composition  $\text{Ti}_2\text{Na}(\text{PO}_4)_3$ , resembling both in form and composition the stannic compound formed under similar circumstances. An attempt to prepare the corresponding tetragonal titanic compound  $\text{TiNa}_2(\text{PO}_4)_2$  was unsuccessful.

C. E. G.

### The Oxychlorides of Antimony. By W. CARLETON WILLIAMS (*Chem. News*, xxiv, 224).

WHEN one molecule of phosphorus pentoxide is heated with three molecules of pentachloride, phosphorus oxychloride is produced. The author has endeavoured to establish a similar reaction in the antimony series, and to prepare the missing oxychloride corresponding to the phosphorus compound above mentioned.

One molecule of antimony pentoxide (prepared by decomposing the pentachloride with water) was heated with three molecules of antimony pentachloride in a sealed tube to  $140^{\circ}\text{C}$ . On opening the tube, it was found to contain two distinct crystalline compounds. One of these, which was produced in considerable quantity, fused at  $85^{\circ}$ ; the other at  $97.5^{\circ}$ , and advantage was taken of this circumstance to effect their separation.

The more fusible compound yielded by analysis 43.46 p. c. Sb, and 54.75 Cl, agreeing nearly with the formula  $\text{Sb}_3\text{Cl}_{13}\text{O}$ , which requires 43.39 Sb, 54.71 Cl, and 1.90 O. It may be regarded as a triple molecule of the pentachloride in which 2 at. Cl are replaced by O. The evidence that this is a definite compound and not a mere mixture of pentoxide and pentachloride, is deduced from the fact, that the latter substance is not dissolved out by washing with carbon disulphide.

The less fusible oxychloride gave by analysis 53.84 p. c. Sb, and 36.58 Cl, leading to the formula  $\text{Sb}_3\text{Cl}_7\text{O}_4$  (calc. 53.93 Sb, 36.62 Cl, 9.44 O.), or 3 molecules of antimony pentachloride in which 4 atoms of oxygen replace 8 of chlorine.

From the above results it is clear that the simple phosphorus oxychloride is not reproduced under similar circumstances in the antimony series, but that more complicated compounds are obtained.

The author has also examined some of the oxychlorides derived from antimony trioxide. He confirms Sabanejeff's formula for "powder of algaroth,"  $\text{Sb}_4\text{Cl}_2\text{O}_5$ ; but is of opinion that the substance produced by the sole action of boiling water upon the trichloride consists of 10

molecules of the above mentioned oxychloride united with 1 molecule of trichloride, the latter being removable by carbon disulphide or ether.

Repeating Schneider's experiments, by heating 15 parts of antimony trichloride with 1 part of trioxide in a sealed tube, he obtained a crystalline oxychloride of very complex composition, the percentage results of which led to a formula differing altogether from the one originally assigned to it by Schneider. It probably contained a proportion of trioxide or trichloride, from which it seemed impossible to purify it.

J. W.

**Observations on the Solubility of Silver Chloride (referring to a recent Communication made by Stas).** By J. PIERRE (Compt. rend., lxxiii, 1090).

WHEN solution of silver nitrate is added drop by drop to concentrated hydrochloric acid, the precipitate formed disappears so rapidly that it sometimes escapes observation altogether. The weight of the silver chloride dissolved may exceed one-half per cent. of the weight of the hydrochloric acid employed. The subsequent addition of water does not easily reprecipitate the whole of the chloride.

When nitric acid is distilled over a small quantity of silver chloride in the state of powder, the latter disappears gradually; this is, however, not a simple solution, because, at the end of the operation, crystallised silver nitrate is found in the retort instead of the chloride.

R. S.

## Mineralogical Chemistry.

**The Connection of certain Phenomena with the Origin of Mineral Veins.** By J. ARTHUR PHILLIPS (Phil. Mag. [4] xiii, 401—413).

THE author introduces the subject by referring to the work of Baron von Herder, published in 1838, in which is given an enumeration and classification of the causes by which mineral veins are supposed to have been produced. Without entering into any detailed description, more especially as the terms employed by von Herder in defining the various modes of formation are sufficiently explicit to mineralogists, we may summarize them as follows:—

1. Theory of contemporaneous formation.
2. Theory of lateral secretion.
3. Theory of descension.
4. Theory of ascension.

The last theory may be divided into four sub-classes—*a.* By infiltration. *b.* By aqueous vapours. *c.* By sublimation. *d.* By injection.

The formation of veins has been the subject of much speculation since the date above referred to, and various authors have either advanced new theories or have advocated more or less important modifications of



those before promulgated. The author quotes the researches of Werner, R. W. Fox, and others, which he considers at least worthy of consideration, though probably incapable of explaining satisfactorily the phenomena in question; he afterwards adds his own testimony in support of the theory that the majority of lode fissures have been produced and subsequently converted into mineral veins by volcanic or plutonic agency.

The authority of Sir Charles Lyell, Daubrée, Senarmont, Von Richthofen, and others, is advanced in favour of this theory, their evidence tending to show that lodes occur more frequently in rock formations of great age than in recent ones; that certain classes of them, such for instance as oxide of tin, are found only in the oldest rocks; that mineral veins are most metalliferous near the contact of plutonic and stratified formations, especially where the former send veins into the latter—a circumstance which indicates an original proximity of veins, at their inferior extremity, to igneous and heated rocks; and further, that the principal minerals found in veins such as quartz, spathose iron, red silver ore, &c., may be produced in a crystalline form by the aid of water, heated to temperatures varying from  $130^{\circ}$  to  $300^{\circ}$  C.

The author's own researches upon this subject have been principally directed to prove that great natural causes are at the present moment at work, producing deposits of minerals such as sulphur, silica, iron pyrites, cinnabar, &c., which agree perfectly in their physical and other characteristics with the vein-matter of more ancient lodes, and that although in the present state of our knowledge it may be impossible to explain all the various phenomena which have been observed in connection with the origin and constitution of veins, nevertheless a careful consideration of ascertained facts must lead to the conclusion that true mineral veins have originally existed as fissures, perhaps produced by volcanic disturbances, and have subsequently become filled during the ensuing period of solfataras and hot springs.

The subject is summed up in the following words:—

Firstly.—Metalliferous lodes are more numerous and productive in the vicinity of igneous rocks than elsewhere.

Secondly.—There is abundant evidence of volcanic eruptions having taken place during all periods of geological time.

Thirdly.—Solfatara action and thermal springs are often the latest evidence of volcanic disturbance.

Lastly.—Crystalline quartz, iron pyrites, mercury sulphide, and various other minerals, are at the present time being deposited by solfataras in veins possessing many of the characteristics of ordinary lodes.

In order to ascertain whether waters traversing mineral veins contained any appreciable quantity of the constituents of the lodes through which they passed, the author subjected three specimens, obtained from deep Cornish mines, to careful analysis. They were, however, not found to contain anything beyond the usual saline constituents of spring water; the evidence which it was anticipated might arise from this examination was therefore negative.

J. W.

**Occurrence of Crystallised Boracite in the Salt-beds of Stassfurt.** By B. SCHULTZE (Jahrbuch für Mineralogie, 1871, 844—850).

BORACITE, hitherto found at Stassfurt only in microscopic crystals, has lately been obtained from the residues of the potassium chloride preparation in crystals of three varieties, viz.: 1. Small kidney-shaped druses, consisting of an envelope of transparent greenish crystals about 0.5 mm. in shape, enclosing a bluish or greenish-grey microcrystalline nucleus, composed of crystals of the same kind. 2. Small crystalline groups or nodules, consisting of light green translucent to transparent crystals about 5 mm. long, enclosing a nucleus of white to greenish colour. 3. Larger druses, in which a white, fine-grained nucleus of Stassfurtite gradually passes, towards the surface, into a greenish, fine-grained crystalline mass, surrounded wholly or partially by very small crystalline groups, and a few isolated crystals about 2 mm. in size.

All the crystals are well developed, and show no signs of efflorescence. They exhibit distinctly the combination  $\frac{O}{2} \cdot \infty O \infty \cdot \infty O$ ; in some specimens the face  $-\frac{O}{2}$  may be recognised with a lens; in a few the face  $-\frac{202}{2}$ . The tetrahedron is almost always predominant.

The crystals have a vitreous lustre, no distinct cleavage, a conchoidal fracture, hardness = 7, mean density = 2.91. They contain boric acid and magnesia, with small quantities of ferrous oxide and chlorine, from which and from their morphological and physical characters, it is inferred that they consist of boracite,  $MgCl_2 \cdot 2(3MgO \cdot 4B_2O_3)$ .

Stassfurtite, which has the same composition, and forms the nucleus of some of the boracite druses above mentioned (3), appears to be merely the cryptocrystalline form of boracite.

H. W.

**Astracanite from Stassfurt.** By H. B. GEINITZ (Jahrbuch für Mineralogie, 1871, 856; also by C. Zincken, *ibid.* 883).

THIS mineral, having the composition  $Na_2SO_4 \cdot MgSO_4 + 4H_2O$ , occurs in the Stassfurt salt-beds associated with carnallite and kainite. Two specimens (a) of sp. gr. 2.28 and hardness 2—3; (b) of sp. gr. 2.223 and hardness 3.5, gave the following results on analysis:—

	Calculated,	Found.	
		a.	b.
Na <sub>2</sub> O .....	18.60	18.24	18.50
MgO .....	12.14	12.64	11.96
2SO <sub>3</sub> .....	47.79	47.69	47.97
4H <sub>2</sub> O .....	21.47	21.66	21.44
	100.00	100.23	99.87

The astracanite of Stassfurt differs from that of Astracan Ischl in Upper Austria, and Mendoza, in La Plata, in forming distinct crystals

as well as crystalline masses. The mineral called Simonyite, from Hallstadt, described by Tchernak (Jahrbuch, 1870, 223), is identical with astracanite. This, and the Stassfurt mineral do not give up their water till they are strongly heated, whereas some of the native varieties, that of Ischl for example (blöedite), are described as efflorescent; but this may perhaps arise from admixture of glauber salt or other impurities.

H. W.

**On the Formation of Anhydrite occurring together with Rock-salt.** By G. ROSE (Berl. Akad. Monatsber. 17 Juli, 1871; Jahrbuch für Mineralogie, 1871, 932).

ANHYDRITE often occurs associated with gypsum and rock-salt, in such a manner as to indicate that it is not a primary formation, but has been produced by dehydration of gypsum. That it can be produced in this manner, especially in presence of sodium chloride, has been shown by the experiments of Hoppe-Seyler and of G. Rose, both of whom find that crystallised gypsum, or selenite, heated to  $130^{\circ}$  in a saturated solution of sodium chloride, is converted into a white opaque mass made up of microscopic crystals of anhydrite. Rose also finds that crystals of selenite heated for a short time with solution of sodium chloride in a platinum dish, are converted on the edges into fibrous anhydrite. Powdered gypsum similarly treated is converted into small prismatic crystals of anhydrite; and a concentrated solution of gypsum mixed with an equal volume of concentrated salt-solution and evaporated yields microscopic crystals of anhydrite. Pseudomorphs of anhydrite in the form of gypsum are found at Sulz on the Neckar.

H. W.

**Analysis of Amblygonite (Montebrasite) from Montebras (Dep. of Creuse).** By F. PISANI (Compt. rend., lxxiii, 1479).

THE fluophosphate called montebrasite, lately found in the stanniferous strata of Montebras (p. 892 of last volume) was regarded by Des Cloizeaux as a new mineral species, on the ground of an analysis by Moissenet, which gave 26.5 p. c. F., 21.8  $P_2O_5$ , 38.2  $Al_2O_3$ , 6.5 lithia and 6.70 soda, with small quantities of lime and quartz. Pisani, however, finds that its composition is as follows:—

F.	$P_2O_5$ .	$Al_2O_3$ .	$Li_2O$ .	$Na_2O$ .	Manganese oxide.	Loss by ignition.
8.20	46.15	33.82	8.10	2.28	0.40	1.10 = 100.05

This, with a slight difference in the amount of soda, is the composition of amblygonite, with which the Montebras mineral likewise agrees in appearance, hardness, density ( $3.11$ ), angle of cleavage ( $105^{\circ}$ ), and pyrognostic properties. It is, therefore, not a distinct species, but identical with amblygonite, which has hitherto been found only in Saxony and the United States.

H. W.



**The Beauxites of the Alpine Chain (Bouches-du-Rhône),**

By H. COQUAEND (Bull. de la Soc. géol. de France, xxviii, 98; Jahrbuch für Mineralogie, 1871, 940).

THE beauxite occurring in the neighbourhood of Beaux is largely employed for the preparation of aluminium and alumina. There are two varieties of it distinguished as ferruginous and aluminiferous; in the former the ferric oxide varies from 25 to 60 p.c. A ferruginous beauxite from the neighbourhood of Nas de Gilles yielded by smelting 42 p.c. iron, and was found by analysis to contain 4 p.c. silica, 18 alumina and tetanic oxide, 60 ferric oxide, and 18 water with lime. The aluminiferous beauxite consists, according to five analyses by Sainte-Claire Deville, of—

	I.	II.	III.	IV.	V.
Silica .....	20·7	2·8	4·8	—	2·0
Titanium .....	3·2	3·1	3·2	—	1·6
Ferric oxide .....	3·8	25·3	24·8	34·9	48·8
Alumina .....	58·1	57·6	55·4	30·3	33·2
Calcium carbonate ..	trace	0·4	0·2	12·7	5·8
					(corundum)
Water .....	14·2	10·8	11·6	23·1	8·6
	<u>100·0</u>	<u>100·0</u>	<u>100·0</u>	<u>100·0</u>	<u>100·0</u>

I and II from Beaux; III from Allauch, near Marseilles; IV from Beaux; V from Calabria.

Both varieties of beauxite are compact, earthy, and pisolithic.

The beauxite in the neighbourhood of Beaux is situated between the lowest zone of the tertiary formation and the upper chalk; its origin in this new cretaceous zone is attributed to mineral springs.

H. W.

**Mineralogico-Chemical Observations: Marceline.—Constitution of Silica.** By F. v. KOBELL (Jahrbuch für Mineralogie, 1871, 884.)

MARCELINE, a manganese ore from St. Marcel in Piedmont, related to braunite, but differing from it by containing a silicate, was found by Damour to consist of:

MnO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MnO.	FeO.	CaO.	MgO.	SiO <sub>2</sub> .
66·68	10·04	8·79	1·30	1·14	0·26	10·24 = 98·45

On dissolving it in strong hydrochloric acid, gelatinous silica separates out. On the hypothesis that silica is SiO<sub>2</sub>, the silicate contained in this mineral has been regarded as RO.SiO<sub>2</sub>, and as an isomorphous substitute of MnO.MnO<sub>2</sub>, which involves the assumption that SiO<sub>2</sub> and MnO<sub>2</sub> are isomorphous; this view is, however, inconsistent with the known forms of silica and polianite. With regard to the constitution of silica, the author points out that the formula SiO<sub>2</sub> is not supported by the crystalline forms of silica and of the oxides of

tin and titanium,  $\text{SnO}_2$  and  $\text{TiO}_2$ , inasmuch as, amidst all the multifarious forms of quartz-crystals scattered over the earth, not one has been found exhibiting isomorphism with cassiterite or rutile, anatase or arkansite, neither has stannic or titanic oxide ever been known to assume any of the hexagonal forms of quartz. On the other hand, the replacement of silica by alumina appears to be probable in many cases, and as this replacement is not easily reconciled with the formula  $\text{SiO}_2$ , Kenngott has suggested that  $\text{Al}_2\text{O}_3$  may (like manganic oxide) be composed of  $\text{AlO}$  and  $\text{AlO}_2$ , the former being capable of replacing  $\text{RO}$ , and the latter of replacing  $\text{SiO}_2$ . This view serves to reconcile the differences in the formulæ of many mineral species as chlorite, ripidolite, &c., but it is purely hypothetical, inasmuch as neither  $\text{AlO}$  nor  $\text{AlO}_2$  is known in the separate state.

The specimen of Marceline examined by F. v. Kobell exhibited drusy cavities filled with needle-shaped crystals of rhombic aspect, ruby-coloured by transmitted, and having a black metallic lustre by reflected, light. They were too small in quantity for complete examination, but exhibited with borax the reaction of manganese. They are very probably the silicate whose presence is revealed by the analysis, and if so, their mode of occurrence, as well as their crystalline form, cannot well be reconciled with the supposed isomorphous replacement.

H. W.

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**New Mode of Occurrence of Tridymite.** By A. STRENG (Jahrbuch für Mineralogie, 1871, 933.)

THE occurrence of tridymite has hitherto been almost wholly confined to trachytic rocks, in which it was first discovered by G. v. Rath. G. Rose afterwards found it in several opals. A. Streng has also found it in another crystalline rock, viz., an orthoclase-porphry or porphyrite in the neighbourhood of Waldböckelheim. This rock consists of a light-grey or brown ground mass, inclosing numerous small, narrow, white, or reddish crystals of triclinic felspar, and somewhat broader, more isolated crystals of white or reddish orthoclase, also dull dark-brown crystals, probably of decomposed hornblende. The rock appears, therefore, to be intermediate between orthoclase-porphry and porphyrite (which consists of a fine-grained ground-mass, in which are embedded crystals of calcio-sodic felspar and hornblende), and to form the transition-term from the one to the other. Its ground-mass is traversed by numerous very irregular cavities, from 1 to 4 centimeters long, and often equally broad, and these cavities are lined with great numbers of small crystals of tridymite in the characteristic forms of this mineral, namely, six-sided tablets, exactly like those from the trachyte of the Drachenfels, and mostly united in twins, triple crystals, &c., and intersecting one another in the manner described by G. v. Rath. The crystals are about a millimeter in diameter, and exhibit distinctly only the prism and the basal pinacoid; the pyramidal faces are not distinctly recognisable. The crystals are infusible before the blow-pipe; some of them are surmounted by small, well defined octohedrons of magnetic iron oxide, which does not occur in the ground mass.

The rock above mentioned contains a larger proportion of tridymite than any trachyte. According to Laspeyres, the porphyrites of the Gienberg, near Waldbökelheim, in the neighbourhood of the Bahnhof, contain 64·49 p.c., or, in the dried state, 65·8 p.c. silica. In the trachyte of the Drachenfels the silica amounts to 64·67 p.c.; in that of San Cristobal, in Mexico, in which tridymite was first found, to 61·03; and in the domite of Auvergne to 63·69 p.c. Hence it appears that these rocks agree in their proportion of silica with orthoclase porphyry and porphyrite, and that tridymite occurs, not in the most siliceous rocks, but chiefly in those which do not contain a larger proportion of silica than oligoclase, and consequently do not generally contain quartz. The occurrence of tridymite in small cavities is likewise common to all the rocks in which it has been found. Its occurrence in trachyte and in non-quartzose orthoclase-porphyry, or porphyrite, affords further evidence of the already well-recognised similarity of the members of the porphyritic and trachytic series of rocks.

H. W.

**The Tachylite and Dolerite of the Sababurg in Hesse.** By H. MÖHL (Jahrbuch für Mineralogie, 1871, 885).

THE Sababurg, a basaltic mountain which, together with others, overlooks the Reinhardswald, a sandy table-land situated between the Oberweser and the mouth of the Diemel, consists mainly of a true felspathic dolerite, together with tachylytic and basaltic rocks. The dolerite (*a*) and tachylyte (*b*) have the following composition:

SiO<sub>2</sub>. TiO<sub>2</sub>. Al<sub>2</sub>O<sub>3</sub>. Fe<sub>2</sub>O<sub>3</sub>. FeO. MnO. CaO. MgO. K<sub>2</sub>O. Na<sub>2</sub>O. P<sub>2</sub>O<sub>5</sub>. H<sub>2</sub>O.

*a.* 54·62 1·26 16·42 3·92 7·88 0·33 7·23 2·08 1·35 4·23 0·83 1·24 = 101·39  
*b.* 54·93 0·28 19·36 3·68 6·48 0·06 6·27 2·16 0·73 3·14 0·04 2·16 = 99·29

The paper contains an elaborate description of the physical and microscopic characters, and the mode of occurrence of these several rocks.

H. W.

**Rammelsbergite.** By F. SANDBERGER (Bayer. Akad. Ber. 1 Juli, 1871; Jahrbuch für Mineralogie, 1871, 935).

THIS mineral, the rhombic form of nickel diarsenide, NiAs<sub>2</sub>, hitherto found only at Schneeberg in Saxony, has lately been found at Wittichen in Baden. A specimen analysed by A. Hilger gave results agreeing nearly with the former analysis by E. Hofmann (*Rammelsberg's Mineralchemie*, p. 21).

	As.	Ni.	Fe.	Bi.	Cu.	Co.	S.
Hilger ....	68·30	26·65	2·06	2·66	trace	trace	trace = 99·67
Hofmann ..	71·30	28·14	—	2·19	0·50	—	0·14 = 102·27

Deducting the bismuth, and reckoning the iron as nickel, both analyses lead to the formula NiAs<sub>2</sub>, which requires 72·15 p.c. As, and



27·85 Ni. The mineral becomes covered by weathering with a very light green crust, appearing under the microscope as a mixture of glistening white octohedrons of arsenious oxide, and green lustreless nickel arsenate (nickel-bloom).

In the specimen analysed by Sandberger the rammelsbergite is coated with a crust of steel-grey smaltine,  $\text{CoAs}_2$ , which is intimately mixed with quartz, very hard, and shoots out on the surface into larger crystals,  $\infty \text{O}\infty$  . O. Besides cobalt and arsenic, it contains a large quantity of iron, with very little nickel, copper, and sulphur. It is evidently identical with the mineral from the Sauschwart mine at Schneeberg, analysed by E. Hofmann, and containing 0·66 p. c. S, 1·39 Cu, 0·01 Bi, 70·37 As, 11·71 Fe, 1·79 Ni, and 13·95 Co. The surface of separation of the two minerals does not exhibit a regular curvature, as if one of them had been deposited over the other, but is irregular and jagged, as if the arsenides of the several metals had been first precipitated together, and separated by subsequent molecular action, in such a manner as to concentrate the nickel in the interior. Precisely similar appearances are presented in the occurrence of copper-nickel with smaltine and cloanthite, the copper-nickel forming the irregularly bounded nucleus of a spheroid, and containing only traces of cobalt, which, on the other hand, is concentrated with the iron, and without any nickel, in the outer crust. A specimen from Wittichen was found to contain—

	Ni.	CO.	Fe	S.	As.
In the nucleus (copper-nickel) ..	43·86	trace	0·67	1·18	53·49
In the crust (smaltine) .....	8·52	10·11	5·05	4·71	69·70

H. W.

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**Blende Crystals from Unkel.** By A. v. LASAULX (Jahrbuch für Mineralogie, 1871, 937).

THE crystals are rhombic dodecahedrons, sometimes of considerable size, and having their faces thickly covered with smaller blende crystals, all disposed parallel to one another, so that the reflected images from their dodecahedral faces coincide with those from the faces of the large crystal. The small crystals are very irregularly developed, but exhibit the face  $3\text{O}3$  in combination with  $\infty \text{O}$ , forming a four-faced acumination of its octohedral summits, by which it is easy to recognise the situation of the faces of the crystal. The occurrence of  $3\text{O}3$ , and of the subordinate faces  $\infty \text{O}\infty$  and O, marks out the independent form of the small crystals, showing that the faces of the large crystal have not been corroded, but are covered with a layer of smaller crystals in regular order.

H. W.

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**Bismuthite from St. José in Brazil.** By FR. v. KOBELL (Bayer. Akad. Ber. 6 Mai, 1871; Jahrbuch für Mineralogie, 1871, 939).

THIS mineral (hydrated bismuth carbonate) occurs, together with joseite, at St. Jaò (José) di Madureira, in Brazil, in small stratified lumps, which appear to enclose a number of pseudomorphous

prismatic crystals; the recently fractured surface exhibits, under the lens, the appearance of pyromorphite. Very soft. Sp. gr. = 5.66. The powder is grass-green, and retains its colour when boiled with potash, but is immediately blackened by ammonium sulphide. Heated in a tube before the blowpipe, the mineral decrepitates, gives off a large quantity of water and becomes brownish. On charcoal it melts very easily, and is reduced with intumescence. It dissolves in nitric acid, especially when heated with evolution of carbonic anhydride. Fused on charcoal with sulphur, and then with potassium iodide, it yields a bright red deposit of bismuth iodide, which, as F. v. Kobell has shown, affords an excellent test for the presence of bismuth.

H. W.

**Pucherite.** By A. FRENZEL (J. pr. Chem. [2], iv, 227—231 and 361).

THIS mineral is a bismuth vanadate found in a mine at Schneeberge in Saxony, in small crystals of the rhombic system, mostly recognisable only with the lens. The following combinations have been observed:—

1.  $\infty P . oP$ , and  $oP . \infty P$ .
2.  $\infty P . \check{P}\infty$ .
3.  $\infty P . oP . m\check{P}n$ .
4.  $oP . \infty P . \check{P}\infty . m\check{P}n$ , and  $\infty P . \check{P}\infty . m\check{P}n . oP$ .

Cleavage perfect parallel to the base. Lustre vitreous to adamantine. Colour reddish-brown to brownish-red. Streak yellow. Opaque to translucent. Sp. gr. 5.91 (the determination, however, is too low, as the analysis showed a certain admixture of quartz). Hardness near that of fluorspar.

The mineral decrepitates violently before the blowpipe; melts on charcoal, and gives a yellow deposit of bismuth oxide, and when fused on charcoal with sodium carbonate, yields metallic bismuth. With borax and phosphorus salt, it gives the reactions of vanadium.

It dissolves easily in hydrochloric acid, with evolution of chlorine, forming a deep red liquid, which becomes green on standing or immediately on dilution with water; when poured into a large quantity of water, it yields a yellowish white precipitate of basic bismuth chloride containing vanadic acid; with ammonia it yields a yellowish to greyish-white precipitate of vanadiferous bismuth hydrate.

Analysis gave the following results:—

	Calculated.		Found.	
			a.	b.
$Bi_2O_3$ .....	464.0	71.76	73.39	72.93
$V_2O_5$ .. . . .	182.6	28.24	27.31	27.07
$Bi_2O_5.V_2O_5$ ..	646.6	100.00	100.70	100.00

Pucherite is therefore a monobasic vanadate of bismuth. A small

quantity of phosphoric acid was detected in it by the reaction with molybdc acid.

The separation of vanadium from bismuth cannot be completely effected either by fusion with sodium carbonate or by precipitating the bismuth as basic chloride. Another method is to fuse the mineral with potassium cyanide, weigh the resulting bead of bismuth, and estimate the vanadic acid in the alkaline solution; but this method also yields too little bismuth by about 2 p. c.

H. W.

### Hypochlorite. By A. FRENZEL (J. pr. Chem. [2], iv, 355—361).

THE name hypochlorite has been applied to certain varieties of green iron-ore occurring massive or earthy at Schneeberg, Johanngeorgenstadt and Bräunsdorff, in Saxony. The massive hypochlorite of Schneeberg has a crystallo-granular texture, siskin-green or yellowish-green colour, hardness 6, sp. gr. 2·93—3·0, and even to flat-conchoidal fracture. The Bräunsdorf mineral has a siskin-green colour, hardness 6, sp. gr. 2·81; both have the aspect of hornstone, and pass into the earthy condition, which transformation may sometimes be observed in a lump of the massive mineral. Thin sections of both minerals when examined by the microscope, exhibit in the midst of a greenish opaque substance which forms the principal part, brightly polarising portions (quartz) together with brownish needles arranged in spherical groups. Their composition, according to Frenzel's analyses, is also analogous:

	SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Sb <sub>2</sub> O <sub>3</sub> .	Bi <sub>2</sub> O <sub>4</sub> .	P <sub>2</sub> O <sub>5</sub> .
Schneeberg* ..	88·45	6·00	—	4·76	—
Bräunsdorf....	86·00	7·8	5·0	—	trace

These numbers seem to indicate that the hypochlorites in question are mixtures of silicate of bismuth or antimony, with quartz, ferric oxide, and very small quantities of ferric phosphate.

The earthy variety of antimony hypochlorite is similar in constitution to the massive variety. An earthy crust scraped from a lump of the latter and quite free from foreign admixtures, gave by analysis 78·0 p. c. silica, 11·4 ferric oxide, 7·3 antimonious oxide, and 1·0 water. The earthy bismuth-hypochlorite, on the other hand, differs considerably in constitution from the massive. Pure lumps of it, of hardness 1—2, gave 23·08 p. c. silica, 33·33 ferric oxide, and 43·26 bismuth-oxide, agreeing nearly with the formula,  $\text{Bi}_2\text{O}_3 \cdot 2\text{Fe}_2\text{O}_3 \cdot 4\text{SiO}_2$ , or perhaps  $\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2 + 2\text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2$ , which requires 23·44 p. c. silica, 31·25 ferric oxide, and 45·31 bismuth oxide.

The lump from which this analysis was made exhibited a crystalline structure when broken, and cavities in it were found to be lined with small indistinct apparently monoclinic crystals rather harder than the surrounding parts. As this compound differs entirely from Schüller's

\* Schüller analysed the Schneeberg mineral with very different results, viz., 50·34 SiO<sub>2</sub>, 14·65 Al<sub>2</sub>O<sub>3</sub>, 13·08 Bi<sub>2</sub>O<sub>3</sub>, 10·54 FeO, and 9·62 P<sub>2</sub>O<sub>5</sub> (Dana's Mineralogy, ii, 182).



hypochlorite, Frenzel designates it by a distinct name, bismutho-fer-rite. The hornstone-like mixtures may be provisionally distinguished as bismuth and antimony hypochlorite.

H. W.

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## Organic Chemistry.

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**Preparation of Absolute Alcohol.** By E. ERLÉNMEYER (Ann. Ch. Pharm., clx, 249—250).

MENDELEJEFF (*Zeitschr. für Chem.* 1865, 260), who has found quick lime superior to all the other substances in use for dehydrating alcohol, states that to obtain the alcohol absolute, spirit of not more than .792 sp. gr. must be taken, and its digestion over the quick lime continued for not less than two days, or else for a few hours at 50°—60°. Even then, on distilling, only the middle portions are found to be anhydrous.

By boiling the spirit with the lime in a vessel fitted with inverted condenser, for  $\frac{1}{2}$ —1 hour and then distilling, the whole product obtained is anhydrous. If the spirit contains more than 5 per cent. of water, it is only necessary to repeat the treatment with lime two or more times. But with weak spirit, care must be taken at first not to fill more than half the space occupied by the spirit with lime, as otherwise the vessel may be broken by the slaking of the lime.

In this way several litres of spirit may be converted in a few hours into absolute alcohol.

E. D.

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**Constitution of Allyl Alcohol.** By ED. LINNEMANN (Ann. Ch. Pharm., clx, 251—252).

THE author has ascertained that the nitrites of the amine-bases yield by their decomposition an alcohol always containing one methyl group more than the original amine, provided the nature of the amine permits of the formation of a new methyl group, the amount of carbon remaining unchanged. Thus, from normal propylamine, isopropyl alcohol is obtained; from normal butylamine, isobutyl alcohol; and from isobutylamine, trimethyl-carbinol. But where the nature of the amine does not permit of the formation of a new methyl group, the decomposition of the nitrite of the amine produces the corresponding alcohol: thus, isopropylamine gives isopropyl alcohol, and trimethylcarbinolamine gives trimethylcarbinol.

Now if allyl alcohol contains the methyl group, the nitrite of allylamine must yield by its decomposition the original allyl alcohol, possessing all its known properties, or it will produce acetone. But if allyl alcohol does not contain the methyl group, there must be produced a new alcohol different from the already known allyl alcohol, and containing the methyl group, or, should this be incapable

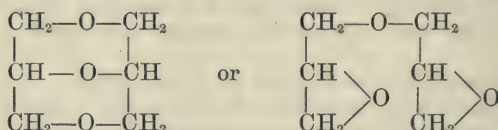
of existing, of an isomeric body such as propylene oxide or propyl aldehyde.

E. D.

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**On the so-called Glycerin Ether.** By H. v. GEGERFELT (Deut. Chem. Ges. Ber. iv, 919).

IN the preparation of allyl alcohol from glycerin, a residue is obtained consisting of the unaltered glycerin and another body separable by repeated distillation. When pure, this substance distils between 170° and 172°, and is a colourless thickened fluid, miscible with alcohol or ether in all proportions, and also with its own bulk of water. On analysis it is found to have the formula  $C_6H_{10}O_3$ . Probably it is identical with the substance obtained by Linnemann and Zotta (*Ann. Ch. Pharm., Suppl.* viii, 254) by heating glycerin with calcium chloride, and only isomeric with the monoallylin of Tollens, the former product boiling at 169°—173°, the latter at about 240°. Either of the formulæ—



might be attributed to this body. Phosphoric chloride, nascent hydrogen, and strong hydrochloric acid have no action on it.

C. R. A. W.

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**Correction to a Note on Bryonicin.** By L. DE KONINCK and P. MARQUART (Deut. Chem. Ges. Ber., iv, 921).

THE substance termed bryonicin, recently extracted from the roots of *Bryonia dioica*, is identical with nitronaphthalene.

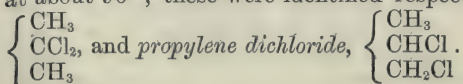
C. R. A. W.

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**Action of Chlorine on Isopropyl Chloride.** By C. FRIEDEL and R. D. SILVA (Compt. rend., lxxiii, 1379—1383).

ISOPROPYL CHLORIDE (B. P. 36°) was prepared by heating isopropyl iodide with excess of mercuric chloride in sealed tubes. The iodide prepared from glycerin, and from isopropyl alcohol obtained from acetone, gave identical results.

Isopropyl chloride was submitted to the action of chlorine in sunlight in a flask cooled by ice; the operation was occasionally interrupted, the product fractioned, and only the portion boiling below 60° again treated with chlorine. Finally, *two* principal products of the same composition,  $C_3H_6Cl_2$ , were obtained, the one boiling at about 70°, the other at about 96°; these were identified respectively with *methylchloracetol*,



Heated with silver benzoate the former furnishes the benzoate  $\text{CH}_2\text{C}(\text{C}_7\text{H}_5\text{O}_2)_2\text{CH}_3$ , in well formed monoclinic octohedrons. Propylene dichloride similarly treated remained for the greater part unaltered, and no corresponding benzoate was formed.

The authors confirm Linnemann's observation that the action of bromine on isopropyl bromide furnishes propylene dibromide boiling at 143. This latter heated with silver benzoate yields propylene benzoate, as a viscous liquid, which boils at  $240^\circ$  under 12–14 mm. pressure, and cannot be crystallised.

By the above action of chlorine in sunlight, more methylchloracetol than propylene dichloride is formed; the amount of the latter varies from two-thirds to one-fifth of the former.

The presence of a trace of iodine facilitates the formation of propylene dichloride at the expense of the methylchloracetol; and by the action of iodine chloride in sealed tubes at  $120^\circ$ , propylene dichloride only is obtained—again an instance that the action of iodine chloride is perfectly different from that of chlorine alone. The authors hold that its first action consists in the formation of an iodo-product; this, however, is acted on by a further quantity, with formation of chloro-product and separation of iodine. No method of producing methylchloracetol alone could be discovered.

H. E. A.

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**Contributions to the History of the Phenols.** By L. DUSART and CH. BARDY (Compt. rend., lxxiii, 1276).

THE authors bring forward a number of experiments which show that although the so-called *phenols* are more closely related in their reactions to the hydrocarbons from which they are derived than are the ordinary alcohols to their hydrocarbons, they nevertheless exhibit reactions characteristic of true alcohols, with this difference, that in overcoming the inertia of their molecules, the elements of time and temperature enter more largely into consideration. Thus:—

Mixtures of phenol and methylic, ethylic, or amylic alcohol saturated with hydrochloric acid, and heated in sealed tubes at  $100^\circ$ , gave the corresponding mixed ethers.

By the action of fuming hydrochloric acid at  $200^\circ$  on phenol, phenyl chloride,  $\text{C}_6\text{H}_5\text{Cl}$ , was formed.

Phenyl acetate,  $\text{C}_2\text{H}_3\text{O}_2\text{C}_6\text{H}_5$ , was obtained by the dry distillation of an intimate mixture of lead acetate and phenolsulphonate,  $(\text{C}_6\text{H}_4\text{OH}\text{SO}_3)_2\text{Pb}$ ; also by the action of fuming hydrochloric acid at  $180^\circ$  on a mixture of acetic acid and phenol.

Sodium or lead phenolsulphonate distilled with potassium cyanide gave benzonitrile.

By the action of aniline on dry sodium phenolsulphonate at  $225^\circ$ , diphenylamine was obtained.

Similarly  $\alpha$  and  $\beta$  naphthyl-sulphonate with aniline gave naphthyl phenylamine.

A mixture of one part aniline chlorhydride, two parts phenol, and one part fuming hydrochloric acid heated at  $250^\circ$  also gave diphenyl-



amine. In the absence of the acid, reaction takes place only above 300°, thus proving the acid to act as etherifying agent.

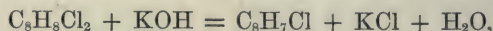
Diphenylamine is formed by passing aniline and phenyl chloride together through a tube heated to approaching redness in a metallic bath; also by the action of sodium in the cold on the above mixture.

Similarly aniline and phenyl iodide (readily obtained by the action of  $\text{CHI}$  on benzene) heated to 280°, yield diphenylamine.

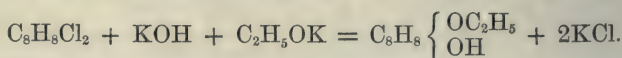
H. E. A.

**Derivatives of Tolylene Dichloride.** By E. GRIMAUZ (Compt. rend., lxxiii, 1383—1385).

By the action of chlorine on methyltoluene (dimethylbenzene) a dichlorinated derivative,  $\text{C}_6\text{H}_4 \begin{Bmatrix} \text{CH}_2\text{Cl} \\ \text{CH}_2\text{Cl} \end{Bmatrix}$  has been obtained. The author has sought to prepare from this, by the action of alcoholic potash, a monochlorotolylene—



but finds that the reaction takes place thus:—



This monethin of tolylene-glycol is a limpid liquid, boiling at 250°—252°. Treated with benzoyl chloride, it is converted into  $\text{C}_8\text{H}_8 \begin{Bmatrix} \text{OC}_2\text{H}_5 \\ \text{OC}_7\text{H}_5\text{O} \end{Bmatrix}$ .

Heated with aqueous potash, tolylene dichloride yields a yellow amorphous product melting above 275°, resembling that obtained by the action of water in sealed tubes at 200° (Compt. rend., June, 1870). These bodies are probably condensed tolylene anhydrides of the formula  $n\text{C}_8\text{H}_8\text{O}$ .

Tolylene dichloride yields a mononitro-derivative on treatment with fuming nitric acid.

H. E. A.

**Action of Hydrogen Bromide on Nitronaphthalene.** By H. BAUMHAUER (Deut. Chem. Ges. Ber., iv, 926).

THE author had previously (*Ann. Chem. Pharm., Suppl.* vii, 204) found nitrobenzene to be reduced to aniline by hydrogen chloride or bromide; as end-products, however, dichloraniline, or di- and tribromaniline were obtained, doubtless formed by the action of the liberated halogen on the first product, aniline.

By the action of aqueous hydrogen bromide on nitronaphthalene at 195°, a mixture of mono- and dibromonaphthalene is obtained, and nitric oxide escapes. Probably the nitro-group is immediately replaced and not reduced—



the monobromnaphthalene being further acted on by the liberated bromine.

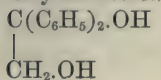
The dibromonaphthalene obtained melts at about  $110^{\circ}$ ; Glaser's two modifications at  $81^{\circ}$  and  $76^{\circ}$ ; so that it is possibly a third form, or perhaps a mixture of brominated naphthalene. The reactions have not yet been confirmed quantitatively.

H. E. A.

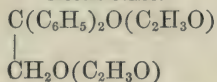
**On Toluylene, Isotoluylene, and Stilbene Alcohols.** By  
H. LIMPRICHT and SCHWANERT (Ann. Ch. Pharm., clx, 177).

BROMOTOLUYLENE,  $C_{14}H_{12}Br_2$ , is heated with the equivalent quantity of silver acetate mixed with glacial acetic acid for some hours in a flask with an inverted condenser attached; silver bromide and the acetic ether of toluylene alcohol are produced; this latter is precipitated by addition of water; and the precipitate, heated with alcoholic potash for 24 hours, is decomposed, with formation of several products separable by successive crystallisations from alcohol. The least soluble is termed *toluylene alcohol*, and has the composition,  $C_{14}H_{12}(OH)_2$ . It has a melting-point varying between  $115^{\circ}$ — $146^{\circ}$ , but all attempts to separate from this product substances of constant melting-point having failed, it appears most probable that it consists of two mutually convertible isomerides; by heating with glacial acetic acid, acetic anhydride, or acetyl chloride, it yields acetic ethers, which similarly exhibit no constant melting-point; thus on heating it to  $180^{\circ}$  with excess of glacial acetic acid for three hours, a product is obtained of composition  $C_{14}H_{12}(C_2H_3O_2)_2$ , and melting at  $85^{\circ}$  in the case of one specimen, at  $87^{\circ}$ — $94^{\circ}$  in the case of others; similarly, by treatment with acetic anhydride in excess for four hours at  $160^{\circ}$ , a product of the same composition is obtained, melting at  $98^{\circ}$  in one case, at  $113^{\circ}$  in another; acetyl chloride forms two compounds after heating at  $100^{\circ}$ , one having the same composition as the above acetic ether, and melting at  $116^{\circ}$ , the other melting at  $57^{\circ}$ , and having the formula  $C_{18}H_{17}O_3Cl$ ; by the action of alcohol at  $140^{\circ}$  on this compound, a syrupy substance is obtained of formula  $C_{30}H_{28}O_3$ ; to these bodies the authors ascribe respectively the following rational formulæ:—

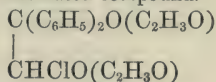
Toluylene alcohol.



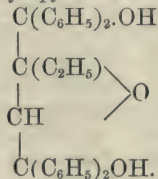
Acetic ether.



Chlorinated compound.\*

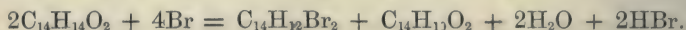


Syrupy substance.



\* Note by Abstractor.—This rational formula contains one atom of oxygen more than that indicated by the analysis.

When toluylene alcohol is oxidized by nitric acid of sp. gr. 1.4, a product is obtained which, after recrystallisation from alcohol, appears to be pure benzoïn melting at  $133^{\circ}$ — $134^{\circ}$ ; benzoïn prepared from bitter almond oil melted at  $137^{\circ}$ , but the melting-point is lowered several degrees by the presence of scarcely perceptible traces of impurities; benzil is also formed by this action. Bromine similarly forms principally benzil, in accordance with the equation—



Alcoholic potash, or soda, at  $180^{\circ}$ — $200^{\circ}$ , decomposes toluylene alcohol, with the evolution of inflammable gases; toluylene, and an oily substance, which on heating gives off vapours smelling like geranium, are produced; dilute sulphuric acid (20 per cent.) abstracts the elements of water, giving a crystalline compound,  $\text{C}_{14}\text{H}_{12}\text{O}$ , melting at  $95^{\circ}$ .

*Isotoluylene alcohol* crystallises in fine needles from the mother-liquors of toluylene alcohol prepared as above described; it melts at  $96^{\circ}$ , and when heated to  $160^{\circ}$  for two hours with acetic anhydride, gives two isomeric acetic ethers, melting respectively at  $135^{\circ}$  and  $96^{\circ}$ . Diluted sulphuric acid (20 per cent.) gives a small quantity of a crystalline compound,  $\text{C}_{14}\text{H}_{12}\text{O}$ , melting at  $95^{\circ}$ , and probably identical with that obtained from toluylene alcohol; the principal product, however, is an oily isomeride of this crystalline compound. Nitric acid of sp. gr. 1.4 converts isotoluylene alcohol into benzoïn, melting at  $135^{\circ}$ .

By acting on benzoïn with alcoholic potash, an isomeride of the above two alcohols is produced, *inter alia*. Zinin, who first discovered this substance, called it *hydrobenzoïn*, but the authors propose to call it *stilbene alcohol*, reserving the term hydrobenzoïn for the other isomeride obtained by the action of nascent hydrogen on bitter almond oil (Zinin, Church, Claus, and Ammann). Stilbene alcohol crystallises in large tabular prisms, melting at  $132^{\circ}$ ; heated with glacial acetic acid to  $176^{\circ}$  for two hours it furnishes the mono- and di-acetic ethers,  $\text{C}_{14}\text{H}_{13}\text{O}_2(\text{C}_2\text{H}_3\text{O})$  and  $\text{C}_{14}\text{H}_{12}\text{O}_2(\text{C}_2\text{H}_3\text{O})_2$ , melting respectively at  $77^{\circ}$  and  $135^{\circ}$ ; acetyl chloride and acetic anhydride give the diacetic ether, melting at  $135^{\circ}$ . Bromine forms benzil and bromo-toluylene, just as with toluylene alcohol; alcoholic potash at  $180^{\circ}$  for some hours forms benzoic acid and toluylene hydrate,  $\text{C}_{14}\text{H}_{14}\text{O}$ ; this latter is further split up into water and toluylene,  $\text{C}_{14}\text{H}_{12}$ . On heating stilbene alcohol with diluted sulphuric acid for half an hour, a crystalline compound,  $\text{C}_{14}\text{H}_{12}\text{O}$ , is produced, melting at  $125^{\circ}$ .

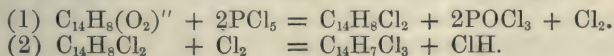
The authors conclude from their experiments that bromotoluylene gives at least two isomerides of the formula  $\text{C}_{14}\text{H}_{14}\text{O}_2$ ; that benzoïn and alcoholic potash give another, with which the hydrobenzoïn of Ammann is probably identical, the isohydrobenzoïn of this chemist being probably a different isomeride. Again, these isomerides differ in the melting point, &c., of the acetyl derivatives, and yield different bodies by the action of sulphuric acid; in some instances, however, both the toluylene and stilbene alcohols form the same products, *e.g.*, by the action of bromine.



**Derivatives of Anthracene.** By C. GRAEBE and C. LIEBERMANN (Ann. Chem. Pharm., clx, 121—145).

WHILST neither Berthelot nor other chemists have succeeded in repeating Harnitzky's synthesis of benzoic acid by means of benzene and carbon oxychloride, and whilst also naphthalene is not acted upon by the latter compound, it yields with anthracene the chloride of anthracene-carbonic acid. In order to prepare this acid, anthracene and liquid carbon oxychloride are heated together in closed tubes for 10—12 hours to 180°—200°. On opening the tubes, currents of hydrochloric acid escape; the contents consisting of yellow crystals mixed with a brown resinous mass are dissolved in a dilute solution of sodium carbonate. On adding an acid to this solution, the anthracene-carbonic acid  $C_{14}H_9.CO_2H$  separates in yellow flakes. It is only sparingly soluble in boiling water, more readily in alcohol, ether, and acetic acid, and crystallises in yellowish needles. When heated, it melts at 206°, at the same time partially decomposing into carbon dioxide and anthracene, a decomposition which begins even already at 150°; on heating it with soda-lime this decomposition is complete. On adding chromic acid to a solution in acetic acid, carbon dioxide escapes and anthraquinone is formed. The silver salt,  $C_{14}H_9.CO_2Ag$ , is a yellow crystalline powder, readily soluble in water. The barium salt  $(C_{14}H_9.CO_2)_2Ba$  separates from the hot aqueous solution in indistinct crystals.

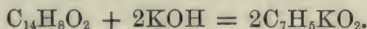
*Action of Phosphorus Pentachloride upon Anthraquinone.*—On heating anthraquinone with phosphorus pentachloride (which was diluted with phosphorus oxychloride) in sealed tubes for some hours to 190°—200°, the following reactions take place:—



The trichlor-anthracene thus obtained is not pure, but always contains higher chlorinated products.

*Anthrahydroquinone.*—On adding a dilute solution of caustic soda to a mixture of anthraquinone and zinc-dust, the liquid assumes a red colour, and the anthraquinone gradually dissolves. On adding an acid to this solution, the product of reduction is obtained as a yellow precipitate, which when exposed to the air is soon reconverted into anthraquinone. To obtain the pure product it has to be precipitated, washed, and dried in an atmosphere of carbon dioxide. The analysis of the compound gave numbers corresponding to the formula  $C_{14}H_8(OH)_2$ , but probably it contains also some anthraquinhydrone  $\left. \begin{matrix} C_{14}H_8OH \\ C_{14}H_8OH \end{matrix} \right\} (O_2)''$ .

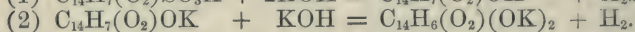
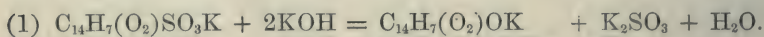
*Decomposition of Anthraquinone by Caustic Potash.*—On heating the two substances together for some time to 250°, the anthraquinone is decomposed, benzoic acid being formed—



*Sulpho-acids of Anthraquinone.*—To obtain *anthraquinone-monosulphonic acid*,  $C_{14}H_7(O_2)SO_3H$ , one part of anthraquinone and 2—3 parts of sulphuric acid are heated to 250°—260°. The free acid is best ob-

tained by decomposing the lead or barium salt with sulphuric acid. It forms yellow scales and is readily soluble in water and alcohol, but nearly insoluble in sulphuric acid. The barium salt  $(C_{14}H_7(O_2)SO_3)_2Ba + H_2O$  forms indistinct yellow crystals, sparingly soluble in cold and a little more readily in hot water. The calcium salt has also a yellow colour, and is much more soluble in water. The sodium salt forms indistinct yellow crystals, and gives with water a yellowish red solution.

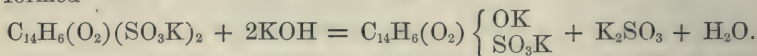
On heating the potassium salt with caustic potash and a little water, the mass assumes gradually a violet colour, and if the heat has been sufficiently high, it contains alizarin, which has been formed according to the equations—



*Anthraquinone-disulphonic Acid*,  $C_7H_6(O_2)(SO_3H)_2$ , is formed by heating anthraquinone with 4—5 parts of sulphuric acid to  $270^\circ$ — $280^\circ$ . It crystallises from an aqueous solution in yellow crystals, and is less soluble than the monosulpho-acid. It is hardly soluble in sulphuric acid. Its yellow salts dissolve in water with a yellowish-red colour, and do not crystallise well. The barium salt is very sparingly soluble in cold water, but a little more readily in hot; the calcium salt is also not very soluble.

On heating one of the salts with potash or soda, alizarin is produced, the formation of which, however, takes place in two stages.

First the red colour of the mixture gradually changes to a dark blue, the potassium salt of an oxyanthraquinone-sulpho-acid being formed—

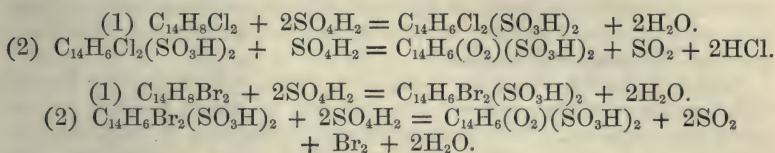


On dissolving some of the dark blue mass with water, and adding dilute sulphuric acid, sulphur dioxide is evolved, and the blue colour of the liquid changes into yellow, but no precipitate is formed.

On heating the blue mass longer, its colour becomes more and more purple, alizarin being now formed, which is obtained as a yellowish red precipitate on adding an acid to the solution of the fused mass. It is easy to find the point when most of the intermediate product is decomposed, by shaking the acid solution with ether, which dissolves only the alizarin, whilst the oxyanthraquinone-sulphonic acid remains in the aqueous solution. On adding an alkali to the latter, the intensity of the blue colours shows whether there is still any of this acid present or not. The crude alizarin obtained by this process always contains some oxyanthraquinone and other colouring matters, which modify the colours produced on mordanted cloth. Moreover, a small quantity of anthraquinone is generally formed by reduction,  $SO_3H$  being replaced by hydrogen; this reduction is more readily effected by heating the sulpho-acids with quick lime, when anthraquinone sublimes in quantities.

When dichlor-anthracene and dibromanthracene are acted upon by sulphuric acid, sulpho-acids are formed, which on heating are converted

into anthraquinone-disulphonic acid. These reactions, which have already been observed by Perkin, take place in accordance with the following equations:—



*Oxyanthraquinone-sulphonic Acid*  $\text{C}_{14}\text{H}_6(\text{O}_2) \begin{Bmatrix} \text{HO} \\ \text{SO}_3\text{H} \end{Bmatrix}$ .—To prepare this compound, the mixture of potash and anthraquinone-disulphonic acid is heated until the formation of alizarin begins.

After cooling, it is dissolved in water, hydrochloric acid is added and the liquid filtered. On adding barium chloride to the filtrate, the yellow barium salt of the sulpho-acid separates out either at once or after evaporation. On decomposing this salt with dilute sulphuric acid, and evaporating the solution, the free acid is obtained in yellow crystals, soluble in alcohol, but not in ether. It forms two series of salts; on dissolving it in caustic potash, a deep blue solution is obtained containing the compound  $\text{C}_{14}\text{H}_6(\text{O}_2) \begin{Bmatrix} \text{OH} \\ \text{SO}_3\text{K} \end{Bmatrix}$ ; on adding hydrochloric acid to this solution, it assumes a yellowish-red colour, the salt  $\text{C}_{14}\text{H}_6\text{O}_2 \begin{Bmatrix} \text{OH} \\ \text{SO}_3\text{K} \end{Bmatrix}$  being formed. The acid barium salt, which has been already mentioned, is tolerably soluble in boiling water, but only sparingly in cold water, and still less in dilute hydrochloric acid. Its yellowish-red solution, like those of the other salts of this acid, becomes yellow on addition of hydrochloric acid, and with baryta-water it gives a blue precipitate  $\text{C}_{14}\text{H}_6\text{O}_2 \begin{Bmatrix} \text{O} \\ \text{SO}_3 \end{Bmatrix} \text{Ba}$ .

*Oxyanthraquinone*  $\text{C}_{14}\text{H}_7(\text{O}_2)\text{OH}$ .—This compound was first observed by Caro and Glaser as a bye-product obtained in the manufacture of artificial alizarin; it is a derivative of anthraquinone-monosulphonic acid, which is always present in the crude sulpho-acids. Oxyanthraquinone may also be obtained by fusing monobromanthraquinone with caustic potash at a low temperature. To isolate the pure compound, the crude alizarin is boiled with water and carbonate of calcium, barium or lead; alizarin lakes are then formed, which are insoluble in water, whilst the salts of the oxyanthraquinone remain in solution. On addition of an acid to the filtrate, a bulky precipitate consisting of microscopic needles is obtained, which, in order to remove traces of alizarin, is again treated with a carbonate as above.

Oxyanthraquinone crystallises from alcohol or ether in fine yellow needles, and sublimes on heating in light yellow scales; in water it is only sparingly soluble.

With bases and carbonates it behaves like alizarin. The salts which it forms with the alkali-metals dissolve in water with a reddish yellow colour; the barium and lead salt form yellow solutions. Concentrated sulphuric acid dissolves it, forming a brownish-red solution, from which



water again precipitates the original compound. It does not dye mordanted cloth, and when heated with zinc dust it yields anthracene.

The authors believe that Schunck's anthraflavic acid, which he discovered in artificial alizarin, is identical with oxyanthraquinone. They have also examined several samples of madder extract for oxyanthraquinone, but could not find any.

*Action of Potash on Alizarin-sulphonic Acid.*—Alizarin was heated with fuming sulphuric acid until on addition of water a clear yellow liquid was obtained. The hydroxides and carbonates of lead, calcium and barium, produce in this solution reddish violet precipitates. On adding a sufficient quantity of baryta water to precipitate only the sulphuric acid, adding caustic potash to the solution, and boiling down, only alizarin was formed, but no purpurin as might have been expected.

C. S.

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**New Method of Synthesis of Organic Acids.** By M. BERTHELOT (Ann. Ch. Phys. [4] xxiii, 212—222).

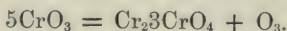
THE relation of acetic acid to acetylene is extremely simple; by the addition of one equivalent of oxygen and one equivalent of water to the former we obtain the latter,  $C_2H_2 + O + H_2O = C_2H_4O_2$ ; similarly, propionic acid from allylene, &c. This relation the author has realised experimentally in the following manner: a gaseous mixture of one volume of acetylene with 20 volumes of air was exposed over dilute potash-solution for six months, at the end of which time the acetylene had for the greater part disappeared, together with a portion of the oxygen; about one-half had become converted into acetic acid, which was isolated; the rest had given rise to a bituminous condensation-product containing C, H, and O.

Acetylene may be more completely converted into acetic acid by the action of *pure* chromic anhydride; the latter was added to an aqueous solution of acetylene, and the mixture allowed to stand for several days. In the presence of little water the action becomes violent, and oxidation to formic and carbonic acid ensues.

The above reagent is far less violent in its action than the ordinary mixture of potassium chromate and sulphuric acid, which diversity in action corresponds to that of the product in the two cases: for whereas with the above mixture the chromic anhydride parts with half its oxygen—



pure chromic anhydride yields up only one-fifth of its oxygen, with formation of chromic chromate—



Allylene was similarly oxidised to propionic acid.

Not only do allylene and its analogues give rise to monobasic acids, but also the more hydrogenated hydrocarbons; thus propylene gave, together with acetone and acetic acid, a notable quantity of propionic

acid; this, probably, is not a direct oxidation-product, but is formed from propylic aldehyde, generated, simultaneously with its metameride acetone, by the oxidation of the propylene.

Isopropylic alcohol gave acetone only, or, in concentrated solutions, the oxidation-products of the latter.

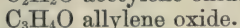
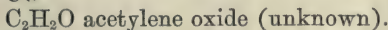
Pinacone, the product of the action of sodium amalgam on aqueous acetone,  $2\text{C}_3\text{H}_6\text{O} + \text{H}_2 = \text{C}_6\text{H}_{14}\text{O}_2$ , was oxidised in the hope of throwing light on its constitution. It has been considered by some to be a dihydric alcohol, and should, if so, yield acids containing at least five, if not the same number of carbon atoms. The author found that acetone was the sole oxidation-product.

Even carbon is attacked by chromic anhydride, and in the cold; besides carbonic anhydride a small quantity of oxalic acid was detected.

The conversion of allylene into propionic acid takes place at two stages:—1.  $\text{C}_3\text{H}_4 + \text{O} = \text{C}_3\text{H}_4\text{O}$ ; 2.  $\text{C}_3\text{H}_4\text{O} + \text{H}_2\text{O} = \text{C}_3\text{H}_6\text{O}_2$ .

The intermediate product (allylene oxide, the isomeride of acrolein) was isolated; it is a mobile neutral liquid, of a penetrating odour, boiling at  $62^\circ$ — $63^\circ$ . It is an extremely stable body; a titrated solution of barium hydrate may be heated with it to  $150^\circ$  without the strength becoming altered; syrupy potassic hydrate does not attack it, even in sealed tubes at  $220^\circ$ , or at  $300^\circ$  (at the end of an hour). It reduces an ammoniacal solution of argentic acetate. Allylene oxide is also formed by the action of isoallylic alcohol (prepared by the action of allylene on sulphuric acid, &c.) on chromic anhydride.

Allylene oxide is the type of a new class of bodies, the homologues of carbonic oxide:—



Experiments to prepare these bodies by the dehydration of the acids of the acetic series were unsuccessful.

H. E. A.

**Formation of Propionic Acid from Carbon Oxide and Potassium or Sodium Ethylate.** By E. HAGEMANN (Deut. Chem. Ges. Ber. iv, 877).

THE author has realised the synthesis of propionic acid according to the equation:—



analogous to that of formic acid from carbon oxide and potassium hydrate (Berthelot).

A current of dry carbon oxide was passed through a solution of 20 grms. potassium or sodium in absolute alcohol for about 20 hours. The acid was finally isolated in the form of silver salt, which analysis proved to have the composition of silver propionate. Simultaneously much formic acid was formed, owing to the unavoidable presence of hydrate in the ethylate. The addition of carbon oxide appears to take place more readily to potassium than to sodium ethylate.

H. E. A.

**Electrolysis of Itaconic Acid.** By G. AARLAND and E. CARSTANJEN (J. pr. Chem. [2] iv, 376—379).

KEKULÉ found that both fumaric and maleic acids give acetylene on electrolysis, but did not determine whether one and the same acetylene was obtained from the two isomeric acids. The authors consider the settlement of this point one of great theoretical interest, but are deterred from its present investigation by the difficulty of obtaining the necessary material. This difficulty does not apply to the next homologue in the series, allylene, corresponding to which three isomeric acids are known: ita-, citra-, and mesa-conic acids, by the electrolysis of which the authors hope to obtain different allylenes, whereof theoretically at least, three isomeric forms are possible.

The gas evolved at the positive pole from a saturated aqueous solution of potassium itaconate produced, after passing through potash, a white flocculent crystalline precipitate in an ammoniacal silver solution; on treatment with mineral acids or gas possessing the characteristic odour of allylene was evolved; this was again passed into a silver solution, and the snow-white precipitate, after rapid drying at  $60^{\circ}$ — $70^{\circ}$  in the dark, was analysed; the numbers obtained agree well with those required by allylene-silver,  $C_3H_3Ag$ . Besides carbonic anhydride and allylene, no gaseous product was detected at the positive pole.

H. E. A.

**Phenaconic and Fumaric Acids.** By L. CARIUS (Deut. Chem. Ges. Ber. iv, 928).

THE following observations prove the *identity* of these two acids:—

*Salts of Phenaconic Acid.*—A solution of normal salt and acid, in the proportions  $(C_6H_3K_3O_6)_2 + C_6H_6O_6$ , evaporated to crystallisation, gave a difficultly soluble salt crystallising in thick monoclinic (?) plates, whilst the mother-liquor contained the normal, very soluble salt. The composition of the first is  $C_{12}H_9K_3O_{12}$ , or  $C_4H_3KO_4$ ; that of the second, which crystallises in prisms, is  $C_6H_3K_3O_6$ . A second acid salt previously described (*Ann. Ch. Pharm.*, cxlii, 154) of the composition  $C_6H_6KO_6$ , was again prepared and analysed; it forms prismatic needles nearly insoluble in water.

*Salts of Fumaric Acid.*—By an exactly similar treatment two acid salts were obtained of the *same* composition and crystalline form as the above, viz.,  $C_4H_3KO_4$  and  $C_{12}H_{10}K_2O_{12}$ , or  $C_6H_5KO_6$ ; this latter is probably  $(C_4H_3KO_4)_2.C_4H_4O_4$ .

H. E. A.

**Phenol Monochloracetate and Amidoacetate.** By E. W. PREVOST (J. pr. Chem. [2] iv, 379).

PHENOL monochloracetate,  $C_6H_5O(C_2H_2ClO)$ , is obtained by heating a mixture of phenol and chloracetyl chloride; it forms silky-glistening needles, insoluble in water, but soluble in alcohol and ether, which melt at  $40.2^{\circ}$ .

Heated with alcoholic ammonia to  $140^{\circ}$  in a sealed tube it is converted into phenol amidoacetate,  $C_6H_5O.(C_2H_2NH_2O)$ , which crys-



tallises in white needles, soluble in water, almost insoluble in alcohol and ether.

H. E. A.

**Formation of Chrysanisic Acid and an Isomeride in the Meta Series.** By H. SALKOWSKI (Deut. Chem. Ges. Ber. iv, 870).

In two previous notices (last volume of this Journal, pp. 555 and 920) the author has shown this acid to be a *dinitroamidobenzoic* acid; he is now able to explain its formation by nitration of nitranisic acid. It is, in fact, the product of the action of ammonia—employed to separate it from simultaneously formed dinitroanisole—on *dinitroanisic* acid. By exhausting the crude nitration-product of nitranisic acid with sodium carbonate solution, &c., dinitroanisic acid was isolated in pale yellow needles melting at 171°–173°. This acid dissolves without decomposition only in very dilute ammonia; when boiled for a few minutes with strong ammonia it is entirely converted into ammonium chrysanisate. Alkalis convert it into dinitro-oxybenzoic acid, identical with that from chrysanisic acid. Chrysanisic acid is consequently a *dinitro-paraoxybenzoic* acid, inasmuch as anisic acid is *paramethoxybenzoic* acid.

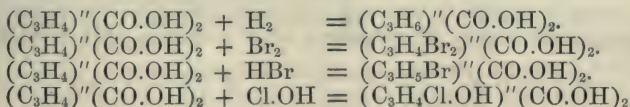
Dinitrosalicylic methyl ether was converted into the ether,  $C_6H_2(NO_2)_2OC_2H_5COOCH_3$ , by the action of ethyl iodide on the silver salt,  $C_6H_2(NO_2)_2OAgOCH_3$ . The product treated with hot ammonia solution gave dinitroamidosalicylic acid, together with the methyl ether of the same; with alcoholic ammonia this latter formed the sole product of the reaction.

*Dinitroamidosalicylic* or *dinitroanthranilic* acid, as it may be termed, or shortly *chrysalylic* acid, is converted into dinitrosalicylic acid, with evolution of ammonia, on boiling with soda. The ethyl ether melts at 135°, the methyl ether at 165°. It bears a great resemblance to its isomeride, chrysanisic acid, and has almost the same melting-point (256°), but the methyl and ethyl derivatives melt about 21° higher than the corresponding chrysanisic derivatives (114° and 144°). Again, the ammonium salt contains one molecule of water, driven off at 100°, whereas that of chrysanisic acid is anhydrous.

H. E. A.

**On the Rational Formula of Chlorocitramalic Acid.** By H. KOLBE (J. pr. Chem. [2], iv, 322).

THIS acid may be viewed as a derivative of pyrotartaric acid, where one proportion of hydrogen is replaced by chlorine, and another by hydroxyl. The following equations show the respective relations that pyrotartaric, citradibromopyrotartaric, citramonobromopyrotartaric, and citraoxychloropyrotartaric acids bear to citraconic acid ( $C_3H_4$ )''( $COOH$ )<sub>2</sub>.



Citraconic acid, heated with liquid nitrogen tetroxide, gave rise to a terrific explosion, which fortunately injured no one.

C. R. A. W.

**On certain Reactions of the Sulpho-Acids of Phenol.** By  
C. GIRARD and G. DE LAIRE (Chem. News, xxiv, 207).

THE replacement of the available hydrogen in aniline by phenyl having been up to the present date invariably unsuccessful, the authors were induced to undertake further experiments upon the subject, owing to the announcement by Messrs. Dusart and Bardy of a general process for the preparation of the secondary monamines of the aromatic series consisting in submitting a primary aromatic monamine to the action of the sulpho-conjugated acids of phenol.

With this view, one molecule of sodium phenol-sulphate was heated in a closed tube with one molecule of aniline to  $280^{\circ}$  for two days. On examining the contents of the tube, no diphenylamine could be found; on the contrary, nearly the whole of the phenol corresponding to the phenol-sulphate was recovered.

On repeating the experiment under similar conditions, but employing an excess of aniline—3 molecules of aniline to 1 molecule of phenol-sulphate—they found that a considerable percentage of diphenylamine was produced. From this circumstance they conclude that the formation of diphenylamine is not due to the substitution of the phenylic residue in phenol for the ammoniacal hydrogen of the aniline, but simply to the action of aniline upon one of its salts.

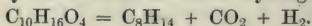
J. W.

**Basicity of Camphoric Acid and Mesocamphoric Acid.** By  
F. WREDEN (Zeitschr. f. Chem. [2], vii, 419—421).

CAMPHORIC acid is generally regarded as a true bibasic acid, but Weyl believes that it has the constitution  $C_9H_{14}(HO)O(CO_2H)$ , being derived from a ketone (*Bull. Soc. Chim.* xi, 109). This, however, is improbable, because it is not reduced either by sodium-amalgam or by zinc and sulphuric acid. Another proof that the old formula  $C_8H_{14}(CO_2H)_2$  is the correct one is that camphoric acid treated with hydriodic acid yields either mesocamphoric acid or the hydrocarbon  $C_8H_{14}$ . The same hydrocarbon appears to be formed by the action of phosphoric acid, Gille's *campholene* being not  $C_9H_{16}$ , but, as Berthelot has pointed out,  $C_8H_{14}$  (*Bull. Soc. Chim.* xi, 109).\*

*Mesocamphoric acid*,  $C_{10}H_{16}O_4$ , is formed by heating one gram of camphoric acid with 6 c.c. of hydriodic acid (sp. gr. 1.6) for two days to  $150$ — $160^{\circ}$ . This acid bears the same relation to camphoric acid as mesotartaric acid to tartaric. It crystallises from water in interwoven needles or warts, melts at 113, and solidifies to a glassy mass. It is optically inactive, and crystallises from oil of vitriol unaltered, whilst common camphoric acid is converted by this acid into the anhydride. By the prolonged action of sulphuric acid a sulpho-acid is formed,

\* Query—What becomes of the hydrogen?



possessing the properties of Walter's sulphocamphoric acid. On heating mesocamphoric acid a sublimate of camphoric anhydride is obtained. The ammonium salts forms an amorphous transparent mass, and the calcium salt could be only obtained in pellicles.

When mesocamphoric acid is repeatedly crystallised from water, or, better still, from dilute alcohol, or when its aqueous solution is boiled for a fortnight with hydrochloric acid, it is converted into a new modification, having all the properties of common camphoric acid, with the exception of being inactive. By treating it with an excess of concentrated hydriodic acid, the hydrocarbons  $C_8H_{14}$ ,  $C_8H_{16}$ ,  $C_8H_{18}$  are formed. On heating 5 grams of common camphoric acid to  $140^\circ$ , with 20 c.c. of hydrochloric acid which fumes at  $0^\circ$ , only mesocamphoric acid is formed, but at  $200^\circ$  the hydrocarbon  $C_8H_{14}$  is obtained.

C. S.

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**On Amido-camphoric Acid.** By F. WREDEN (Zeitschr. f. Chem. [2], vii, 418—419).

*Amido-camphoric anhydride*,  $C_{10}H_{13}(NH_2)O_3$ , is formed by dissolving bromocamphoric anhydride,  $C_{10}H_{13}BrO_3$ , in aqueous ammonia at  $150^\circ$ . It crystallises in needles, is sparingly soluble in boiling water and cold alcohol, but dissolves readily in boiling alcohol. When heated it begins to sublime at  $150^\circ$ , and melts at  $208^\circ$ . Nitrous acid converts it into oxycamphoric anhydride,  $C_{10}H_{13}(HO)O_3$ . The same compound is formed by boiling it with concentrated alkalis, whilst dilute alkalis produce *amido-camphoric acid*,  $C_{10}H_{15}(NH_2)O_4 + H_2O$ , which is more soluble in alcohol than the anhydride, and crystallises in small shining prisms. It loses its water at  $85^\circ$ , and between  $85^\circ$ — $160^\circ$  is changed into the anhydride, which is also formed by the action of nitrous, or of concentrated hydrochloric and sulphuric acids. The calcium salt  $(C_{10}H_{14}NH_2O_4)_2Ca + 2H_2O$  forms transparent prisms, and dissolves readily in water; a normal calcium salt could not be obtained. The copper salt crystallises from water in blue shining needles; the cadmium salt in iridescent pellicles.

Oxycamphoric anhydride,  $C_8H_{13}(OH)C_2O_3$ , is the first representative of a new class of acids containing no carboxyl. That it is really an acid has been proved by preparing salts, ethers, the amide, and the chloride, which latter is decomposed by water into hydrochloric acid and the oxyanhydride, to which the name *camphanic acid* might be given. Kekulé's bromcitraconic anhydride belongs perhaps to the same group of acids.

C. S.

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**New Amido-acids.** By ANNA WOLKOW (Zeitschr. f. Chem. [2], vii, 422—423).

*Benzoyl-paranitrosulphotoluenamide*,  $N[C_7H_6(NO_2)SO_2](C_7H_5O)H$ , is obtained by heating equivalent weights of  $\beta$  nitrosulphotoluenamide and benzoyl chloride to  $145^\circ$ — $150^\circ$  as long as hydrochloric acid is given off. It crystallises in flat prisms grouped in stars, melts at  $130^\circ$ , and is readily soluble in boiling alcohol, but only sparingly in ether and



boiling water. Its solution has an acid reaction, and decomposes alkaline carbonates. The potassium salt  $N[C_7H_6(NO_2)SO_2](C_7H_5O)K$  is anhydrous, readily soluble in water and alcohol, and forms warty needles. The barium salt is insoluble in alcohol, sparingly soluble in water, and forms needles grouped in stars. The calcium salt,  $N(C_7H_6[NO_2]SO_2)(C_7H_5O)Ca + H_2O$ , crystallises from water and alcohol in nodules. The silver compound is a precipitate drying up into a horny mass. It is only slowly attacked by boiling it with hydrochloric acid.

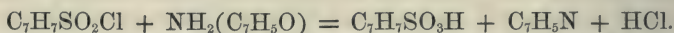
*Benzoyl-paranitrosulphonaphthalenamide*,  $N(C_{10}H_7SO_2)(C_7H_5O)H$ , obtained by an analogous reaction, is sparingly soluble in alcohol, and forms four-sided prisms. In water it is almost insoluble, but it dissolves in acetic acid. The potassium salt is soluble in alcohol and water, and forms crystalline crusts. The barium salt is insoluble in alcohol, sparingly soluble in water, and crystallises in fine needles. Both salts are anhydrous. The calcium salt is more soluble, and forms needles containing  $\frac{1}{2}$  mol.  $H_2O$ . The silver salt is a white precipitate, crystallising from ammonia in needles grouped in stars. The copper, lead, and zinc salts are only sparingly soluble.

C. S.

### On the Action of $\beta$ Toluenesulphonic Chloride upon Amides.

By ANNA WOLKOW (Zeitschr. f. Chem. [2], vii, 421—422).

ON heating equal molecules of this chloride and benzamide to  $135^\circ$ , hydrochloric acid, benzonitrile, and paratoluene-sulphonic acid are formed—

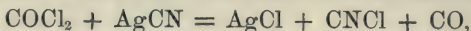


Cinnamide yields, under the same conditions at  $115^\circ$ — $130^\circ$ , hydrochloric acid, the nitrile of cinnamic acid, and the parasulpho-acid, whilst acetamide gives, besides the latter acid, not acetonitrile and hydrochloric acid, but the well known compound of these two bodies.

C. S.

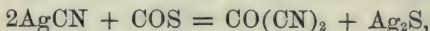
### Preparation of Carbonyl Cyanide. By W. F. GINTL (J. p. Chem. [2], iv, 362).

THE action of carbonyl chloride on silver cyanide takes place according to the equation—



no carbonyl cyanide being formed (see also this Journal, last volume, p. 900.)

Experiments to realise the reaction—



are in progress. Carbonyl cyanide, if obtained, should be convertible into mesoxalic acid; conversely the dehydration of ammonium mesoxalate may possibly yield carbonyl cyanide.

H. E. A.

**On the Behaviour of Monochloracetic Acid to Methylguanidine and other Similar Compounds.** By H. HUPPERT (Deut. Chem. Ges. Ber. iv, 879).

SOME of the reactions of creatine may be explained on the supposition that it is methyluramidoacetic acid. The author, therefore, attempted the preparation of such a body by the action of methyluramine (methylguanidine),  $C_2H_7N_3$ , on monochloracetic acid. The product obtained, however, differs from creatine by containing the elements of one molecule of water more, and has the composition,  $C_4H_{11}N_3O_3$ . It combines directly with hydrochloric acid, forming  $C_4H_{11}N_3O_3.HCl$ ; the platino-chloride,  $C_4H_{11}N_3O_3.H_2PtCl_6$ , forms orange-yellow prisms; with silver nitrate it gives a difficultly soluble compound,  $C_4H_{11}N_3O_3.Ag_2O$ .

Attempts were made to dehydrate the base by the action of gaseous hydrochloric acid at  $100^\circ$ , but under these circumstances two molecules of base lost only one molecule of water. The action of chloracetic acid on methylguanidine is, therefore, analogous to that of the same body on triethylamine, triethylphosphine, piperidine (last volume, p. 147), and strychnine (this volume, p. 79).

Similarly a crystalline derivative was obtained by the action of chloracetic acid on morphine. By the action of chloracetic acid on urea, which might give rise to the formation of hydantoic acid, hitherto only glycollic acid and ammonium chloride have been obtained.

H. E. A.

**Direct Formation of Aromatic Amido-derivatives.** By H. SAL-KOWSKI (Deut. Chem. Ges. Ber. iv, 873).

THE reaction described (see also p. 920 of last volume) consists in the direct replacement of the groups  $OCH_3$  and  $OC_2H_5$  by  $NH_2$  by the action of ammonia. The following substances have thus been converted into the corresponding amido-derivatives:—

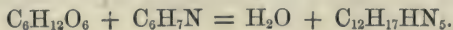
Picric ether,  $C_6H_2(NO_2)_3OC_2H_5$ ; trinitroanisole,  $C_6H_2(NO_2)_3OCH_3$ ; dinitroanisic acid,  $C_6H_2(NO_2)_2OCH_3COOH$ ; ethyldinitroparaoxybenzoic ether,  $C_6H_2(NO_2)_2OC_2H_5COOC_2H_5$ ; ethyldinitrosalicylic methyl-ether; and ethyldinitrosalicylic ethyl-ether.

Certain differences are observable in the mode of action of aqueous and alcoholic ammonia; firstly, that reagent acts most readily in which the resulting compound is most soluble; and in the case of those bodies which also contain alcohol-radicals in the carboxyl group, alcoholic ammonia is without action on this group, whereas aqueous ammonia simultaneously exercises a saponifying action.

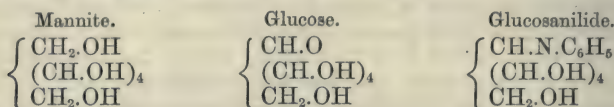
H. E. A.

**The Anilides of the so-called Carbohydrates.** By HUGO SCHIFF (Deut. Chem. Ges. Ber. iv, 908).

WHEN glucose free from moisture is heated with its own weight of aniline, combination and water-elimination ensue.



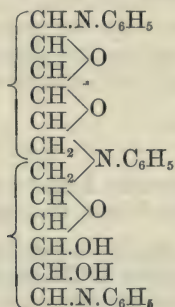
Glucosanilide, the resulting product, is decomposed by water, especially on warming; it may be obtained free from excess of aniline by treatment with benzene, which leaves a solid vitreous substance undissolved. Absolute alcohol dissolves it, but the concentrated solution does not deposit crystals. From the production of this body, the author deduces the following formulæ:—



Aniline acts with more difficulty on cane-sugar, a temperature of  $200^\circ$ — $220^\circ$  being required, whereby caramel is formed and an impure product obtained. From the crude substance a body of composition  $\text{C}_{30}\text{H}_{31}\text{N}_3\text{O}_5$  is isolable, formed by the action of aniline on the caramel first produced.



To this the author attributes the formula—



It forms a platinum salt,  $2\text{C}_{30}\text{H}_{31}\text{N}_3\text{O}_5.\text{H}_2\text{PtCl}_6$ .

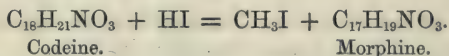
Starch yields only dextrin when heated with aniline: this substance and gum are with difficulty attacked; and glycerin does not give any action even at  $200^\circ$ .

C. R. A. W.

### Contributions to the History of the Opium Alkaloids (Part III).

By C. R. A. WRIGHT (Proc. Roy. Soc. xx, 8).

THIS paper treats of the products obtained by the action of hydriodic acid on codeine in presence of phosphorus. The first action appears to be in accordance with the equation—



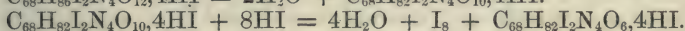
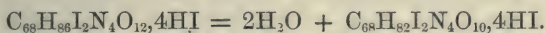
the quantity of methyl iodide evolved being close upon that theoretically obtainable; this evolution of methyl iodide, however, does not take place in the absence of phosphorus, much iodine being set free in this case.



According as the action of hydriodic acid (3 to 5 parts of 50 per cent. HI) and phosphorus ( $\frac{1}{10}$  part) upon codeine (1 part) takes place at 100°, or at higher temperatures, different products are obtained, all of which may be considered as derived from morphine hydriodide by quadruplication of the molecule, addition of  $H_8$  and 2HI to the product, and further alteration of the resulting compound by successive subtractions of the elements of water, and of oxygen. Thus, if the reaction take place at 100°, the product may be viewed as formed by the equation—

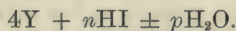


If the mixture be gently boiled so that the boiling point rises to 110°—115°, by the time that methyl iodide ceases to be evolved, the product obtained contains  $2H_2O$  less than this formula; whilst, if the boiling be performed rapidly, so that the boiling point rises to 130°—135°, the end-product contains  $O_4$  less than this latter body: thus—

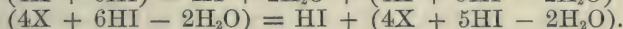
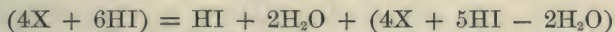


All three substances much resemble each other; they form colourless tarry masses, which rapidly become yellow by exposure to air; when quite dry they do not soften at 100°: water dissolves them with decomposition; from the solution bases derived from the original compounds by subtraction of the elements of HI are obtainable. Their qualitative reactions are identical with those of their derivatives, but utterly different from those of the codeine derivatives previously examined.

Denoting a hypothetical base,  $C_{17}H_{21}NO_3$ , by the symbol X, and another,  $C_{17}H_{21}NO_2$ , by the symbol Y, these three bodies and their derivatives may be all included in one or other of the two general formulæ—



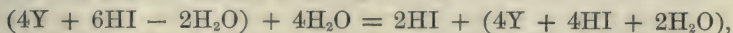
By dissolving the product obtained at 100° ( $4X + 6HI$ ) in boiling water and boiling for some time, flakes of a peculiar microscopical structure are obtained on cooling the liquid; the same product is also got from the substance obtained at 110°—115° by similar treatment, and is formed by the reactions—



On similarly treating the substance thus obtained, the further reaction takes place—



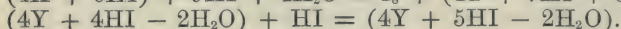
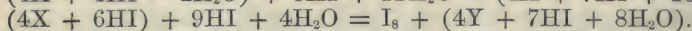
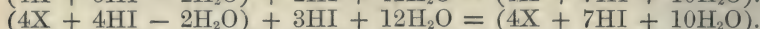
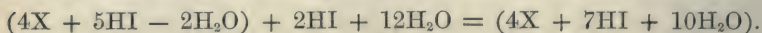
If the original product formed at 130°—135° be similarly treated, it finally furnishes an analogous substance formed by the reaction—



the elements of 4 molecules of water being thus taken up.

On treating the original codeine products with alkalis, the same reactions appear to ensue: thus the free bases ( $4X + HI - 2H_2O$ ), ( $4X + 2HI$ ) and ( $4X - 2H_2O$ ) are obtained. Of these, the one containing no iodine is least soluble in ether, and the one containing most, is the most soluble: they readily absorb oxygen from the air.

On again subjecting these derivatives formed by water or alkalis to the action of hydriodic acid, bodies are produced, not identical with those first obtained from codeine, but still belonging to the same family, and represented by the same general formulæ. Thus the reactions—



have been quantitatively verified.

Names have not been yet given to any of the above bodies on account of their complex constitution, and the slight uncertainty as to the precise formula in one or two cases, arising from the large number of proportions involved, and the unavoidable errors of analysis, &c., in dealing with non-crystalline bodies containing large quantities of iodine, and yielding difficultly combustible carbon on heating.

From the preceding results it is inferred that the action of hydriodic acid wholly polymerises codeine, whereas that of hydrobromic acid does so only partially, products derived probably from one molecule only of codeine being obtainable as well as other bodies derived from four molecules by this agent: hydrochloric acid has not a marked polymerising action on codeine.\*

All three acids eliminate methyl from codeine, forming ultimately bodies containing  $nC_{17}$ .

The carbon groups contained in codeine are in an eminently "unsaturated" condition, inasmuch as they are capable of taking up  $H_2$  for every  $C_{17}$  present in the derivative, and in addition several molecules of  $HI$  and  $H_2O$ , which are held so firmly as not to be lost by heating the products to  $100^\circ$  for days.

C. R. A. W.

### On the Complex Nature of Cathartin. By E. BOURGOIN (Compt. rend. lxxiii, 1449).

CATHARTIN is a product extracted from senna by Lassaigne and Feneulle (*Ann. Ch. Phys.* xvi, 1824), who considered it to be the active principle of the plant. The author has recognised it as a mixture of three distinct substances.

1. *Chrysophanic Acid*.—Obtained by extracting crude cathartin with ether; it is present but in small quantity in senna, but may be at once rendered evident by the formation of a characteristic red colour on the addition of ammonia to an aqueous infusion of the leaves.

\* *Note*.—Researches now in progress appear to indicate that this latter statement requires some modification, products from *polymerised* codeine being apparently obtainable (though with some difficulty) by the action of hydrochloric acid on codeine.—C. R. A. W.

2. *A dextro-rotatory Glucose*.—Cathartin freed from the above acid yields with water a limpid solution, possessing the following properties: 1. It ferments in contact with beer-yeast, giving carbonic anhydride and alcohol. 2. It reduces a cupro-potassic solution. 3. Freed from chrysophanine and colouring matter, it rotates a ray of polarised light to the right. This glucose may be isolated by precipitating with basic lead acetate, and evaporating to dryness after removing the dissolved lead.

3. *Chrysophanine*.—To a strong infusion of senna, after the removal of the mucilagenous matter by alcohol, lead acetate is added, the precipitate decomposed by hydrogen sulphide, the liquid evaporated to a syrup, the syrup treated with alcohol, and the residue dissolved in water, reprecipitated by alcohol, and then dried over sulphuric acid. Thus obtained it is almost white.

H. E. A.

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**Action of Nitric Acid upon Natal Aloes.** By W. A. TILDEN  
(Pharm. J. Trans. [2], ii, 441).

In a paper by Prof. Flückiger on the "Crystalline principles in Aloes," it is stated that when aloin prepared from Natal aloes is treated with nitric acid, oxalic acid only is produced. In opposition to this statement, the author shows that, as he had previously anticipated, picric acid is also one of the products of this reaction.

A small quantity of "nataloin" prepared according to Flückiger's directions, was treated with fuming nitric acid; the liquid was warmed until the action was complete, and then evaporated to dryness. The residue, which undoubtedly consisted chiefly of oxalic acid, yielded, when treated with water, a solution of a bright golden colour, and afforded unmistakeable evidence of the presence of picric acid.

Warmed with potassium cyanide it gave a blood-red solution, and when boiled with chloride of lime, evolved the peculiar disagreeable odour of chloropicrin. A portion of the residue having been mixed with solution of potassium acetate, a crystallisation of small orange needles was obtained. These crystals exploded when heated upon platinum foil, and when dissolved in water and mixed with an ammoniacal solution of copper sulphate, they gave a green precipitate, changing to yellow on the application of heat.

The above reactions are sufficient to indicate the formation of picric acid; it was thought advisable, however, to prepare and analyse one of its salts. The potassium salt, obtained by the action of nitric acid, not upon aloin, but upon the crude drug, gave 14.33 per cent. of potassium. Picrate of potassium contains 14.60 per cent.

J. W.

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**Silicichloroform and its Derivatives.** By FRIEDEL and LADENBURG (Ann. Chim. Phys. [4] xxiii, 430—442).

In two previous memoirs by Friedel and Crafts, on the ethereal and hydrocarbon compounds of silicium, it was pointed out that the con-



stitution of all these compounds is easily explained if silicium is a tetrad like carbon. The present paper deals with some seeming exceptions to this law.

In 1857 Buff and Wöhler, by heating silicium in dry hydrogen chloride, obtained a body to which they ascribed the composition  $\text{Si}_2\text{Cl}_3 + 2\text{HCl}$  ( $\text{Si} = 21$ ). Wöhler afterwards doubled this formula, from supposed analogy with leucone, a product of the action of hydrogen chloride and light on calcium silicide. The formula thus became  $\text{Si}_3\text{Cl}_{10}\text{H}_4$  [ $\text{Si} = 28$ ], and the compound formed from it by the action of water, and supposed by him to be leucone, became similarly  $\text{Si}_3\text{O}_5\text{H}_4$ . As both, however, were impure, the subject remained still doubtful.

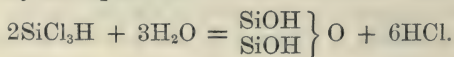
From the volatility of the chloride and its relation to  $\text{SiCl}_4$ , the authors concluded that it must be  $\text{SiHCl}_3$ , derived from the former by substitution, and that previous analyses had been vitiated by the presence (noticed by Wöhler himself) of silicium chloride.

As directed by the discoverers, they passed a slow current of dry hydrogen chloride over crystallised silicium in a green glass tube at a heat below redness. By repeated fractional distillation two portions were isolated, the larger one boiling at  $55^\circ$  to  $60^\circ$ , composed of silicium chloride, the other at  $35^\circ$  to  $37^\circ$ , being the new compound in a pure state. Analysis showed it to have the composition  $\text{SiHCl}_3$ ; and a vapour density determination by Gay-Lussac's method gave 4.64. Theory 4.69.

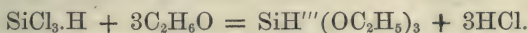
This chloride has all the properties originally described, especially that of exploding, when mixed with air, on the mere approach of a warm body. This, and the disengagement of hydrogen when it is acted on by water, distinguish it from silicium tetrachloride, which it resembles in odour and appearance.

Chlorine at ordinary temperatures decomposes it into hydrogen chloride and silicium tetrachloride. Bromine does not act in the cold, but at  $100^\circ$  the mixture is decolorized, doubtless with formation of the chlorobromide,  $\text{SiCl}_3\text{Br}$ .

*Siliciformic Anhydride*,  $\text{Si}_2\text{O}_3\text{H}_2$ .—The product of the action of water at zero on silicichloroform was formulated by Buff and Wöhler as  $\text{Si}_2\text{O}_3 + 2\text{HO}$  [ $\text{Si} = 21$ ], which agrees with some only of their analyses. It is difficult to obtain it free from silica formed by a secondary decomposition. To prepare it pure, a portion of silicichloroform, boiling at  $34^\circ$  to  $37^\circ$ , and free from silicium chloride, was distilled slowly into pure water at  $0^\circ$ , the delivery tube ending in a funnel to prevent obstruction. The resulting white insoluble body was rapidly filtered off, washed with iced water, pressed, and dried *in vacuo* over oil of vitriol. It may be dried at  $150^\circ$  without decomposition, and then appears as an inflammable white powder resembling silica. Its properties are those originally described. It burns with flame, and dissolves rapidly in potash with liberation of hydrogen. It is decomposed by aqueous ammonia, with separation of silica, and by potash with evolution of hydrogen. The quantities of silica and hydrogen thus obtained show that the formula of the compound is  $\text{Si}_2\text{O}_3\text{H}_2$ . Its formation is represented by the equation—



*Tribasic Siliciformic Ether.*—To prepare this body, alcohol was dehydrated by Friedel and Craft's method, *i.e.*, by heating ethyl silicate with alcohol previously distilled over sodium ethylate. A weighed quantity of the alcohol is added drop by drop to a known weight of pure silicichloroform in a flask with a long neck. On distillation the product begins to come over at  $140^{\circ}$ . If the silicichloroform contain silicium chloride, the new compound will be contaminated with ethyl silicate. The product is subjected to fractional distillation, and is finally obtained as a limpid liquid boiling at  $134^{\circ}$ , easily alterable by moist air, and of an agreeable odour resembling ethyl silicate. It is formed by the following reaction:—



It is decomposed slowly by water, rapidly by potash or ammonia, with brisk evolution of hydrogen. Its vapour detonates when mixed with air. In constitution it is analogous to the body which Kay obtained by acting on sodium ethylate with chloroform, and designated as *tribasic formic ether*.

This ether is distinguished from ethyl silicate by a curious reaction. When it is treated with a fragment of sodium, a little hydrogen is first set free by the moisture adhering to the sodium; then, on gently heating, hydrogen silicide is evolved, and may be recognised by its manner of burning. Flocks of silica are formed, and the inside of the tube becomes coated with a brown amorphous deposit of silicium. By this reaction the authors prepared pure hydrogen silicide, which has not been attained by the ordinary processes.

If the molecule, or 2 vols., of hydrogen silicide contain only one atom of silicium, in oxidising into  $\text{SiO}_2$  it must decompose 2 atoms of water, setting free 4 vols. of hydrogen, in addition to the quantity contained in its own molecule. Now the quantity evolved on decomposing it with potash-ley is actually 8 vols.: the hydrogen silicide must, therefore, contain  $4\text{H}$ , or must be  $\text{SiH}_4$ .

Hydrogen silicide is colourless, not spontaneously inflammable at ordinary temperature and pressure, but explodes on the approach of a warm body, or, when mixed with air, on a mere diminution of pressure. Its formation is thus explained—



The residue is pure ethyl silicate, distilling at  $165^{\circ}$  to  $169^{\circ}$ .

The preceding results thus clear up the apparent exceptions to the tetratomicity of silicium, and exhibit a close analogy between the silicium compounds and those of carbon, the group  $\text{SiH}$  acting as a triad radicle like  $\text{CH}$ . Still each element carries with it into its compounds its own peculiarities, though masked for a time by its union with other bodies.

C. G. S.

**On the Silicoheptyl Series.** By A. LADENBURG (Deut. Chem. Ges. Ber. iv, 901).

SILICOHEPTYL ETHER,  $\text{Si}(\text{C}_2\text{H}_5)_3\text{O}(\text{C}_2\text{H}_5)$ , is permanent in the air, and is not attacked by alcoholic ammonia at  $250^\circ$ . Water does not act on it until the temperature reaches  $200^\circ$ . Among the products of the decomposition is *triethyl-silicol*,  $\text{Si}(\text{C}_2\text{H}_5)_3\text{OH}$ , bearing to silicium the same relation as triethyl-carbinol to carbon.

Acetyl chloride forms, with silicoheptyl ether, acetic ether and *silicoheptyl chloride*,  $\text{Si}(\text{C}_2\text{H}_5)_3\text{Cl}$  (or *silicon-triethyl-chloride*), boiling at  $143.5^\circ$ . Aqueous silver nitrate, and aqueous or alcoholic ammonia, immediately decompose it, aqueous ammonia forming triethyl-silicol; this boils at  $153.5^\circ$ , and has the properties of an alcohol; sodium evolves hydrogen, and forms a solid white amorphous mass; acetyl chloride decomposes it, with evolution of hydrogen chloride, and probable production of the silicol-acetic ether; it is insoluble in water, soluble in ether and alcohol. The corresponding ether,  $\{\text{Si}(\text{C}_2\text{H}_5)_3\}_2\text{O}$ , is possibly among the substances of high boiling point formed by the action of water on silicoheptyl ether, but it has not been isolated.

C. R. A. W.

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## Physiological Chemistry.

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**Relation of Glycogen to Muscular Activity.** By SIGMUND WEISS (Wien. Acad. Ber [2], lxiv, 284—291).

WEISS has adopted the method given by Brücke (*ibid.*, lxiii, 1—9), in estimating the amount of glycogen in muscle, and its relation to muscular activity. The muscles of one leg of a decapitated frog were tetanised by induction currents, while those of the other, the sciatic being cut, remained perfectly at rest. The interesting result of numerous experiments is that muscular action is associated with a marked diminution of the amount of glycogen. In one set of experiments the percentage loss was 24.27; in another it was 28.24; and in a third, where only the larger muscles were compared with each other, the loss was 50.427 per cent.

In relation to this, it was of interest to determine the amount of glycogen in the heart—a muscle in constant activity—as compared with other muscles of the same animal. From a comparison of the amount of glycogen obtained from the heart of a dog with that got from a corresponding mass of muscle from the back, it appeared that the heart, notwithstanding its constant activity, had a store of glycogen amounting to more than two-thirds of that of the other muscles.

Experiments were made with fowls in order to determine whether the amount of muscle-glycogen varies with the food, like liver-glycogen. The results obtained showed that it neither varies so much, nor does it disappear so readily as liver-glycogen when the animal is kept on insufficient food. Hence, even in starvation, muscular energy is retained as long as the store of glycogen lasts.

D. F.



**On the Origin of Fibrin and its Sources in the Organism.**

By JOHN GOODMAN, M.D. (Chem. News, xxv, 4—6 and 17—20).

THE author states that when egg-albumin is suspended in water for some time, it loses the characters of albumin, and assumes those of fibrin. Oxygen does not produce this fibrin, but imparts to it a more fibrous character. A voltaic current passed through water and albumin increases the production of fibrin, but very little is formed by a current passed through pure albumin. The author attempts to prove that fibrin is formed in the body by the action of water absorbed from the stomach on the albumin of the blood.

T. L. B.

**Transformation of Albuminoid Matters into Urea by Potassium Permanganate.** By E. RITTER (Compt. rend., lxxiii, 1219—1220).

O. LOEW (J. pr. Chem. [2], ii) and others having contested the experiments of Béchamp on this subject, the author repeated them, treating albumin, fibrin, and gelatin according to the new method of Béchamp, and succeeded in obtaining urea from them, and in the case of gelatin, another crystalline product also. If the reaction be not carefully watched, so as to stop it at the right moment, the experiment fails.

Béchamp (Compt. rend., lxxiii, 1323—1324) observes that what Ritter (Compt. rend., lxxiii, 1220) calls the *new method*, is the same which he employed fifteen years ago, varying only in the process for extracting the urea; moreover, that he had long ago obtained crystallisable products, other than urea, from albumin, syntonin (muscular fibrin), hæmatocrystallin, and blood-globules.

C. E. G.

**On a Violet Deposit in Urine.** By C. MÉHU (J. Pharm. [4], xiv, 408—412).

MÉHU has examined a violet deposit obtained from a pathological urine. The pigment was found to be composed of a blue and a red substance, but neither of these was obtained in a state of purity. The blue matter was obtained in a crystalline form, and the crystals appeared to be identical with those obtained from a hot alcoholic solution of indigotine. The author thinks that indican is not, as Schunck states, a normal constituent of urine.

T. S.

**Juice of the Larvæ of Cimbex Species.** By A. J. VON ROSSUM (Zeitschr. f. Chem. [2], vii, 423—424).

THE larvæ of *Cimbex variabilis* (living on the leaves of *Alnus incana*) have on both sides of their bodies a series of orifices, from which, on being touched, they squirt a green fluid, which is tasteless and inodorous, and has an alkaline reaction.

On examining its reactions, it was found to consist of a moderately concentrated solution of a proteïde, which has great resemblance to albumin.

The nature of the colouring matter (perhaps chlorophyll) could not be elucidated; alkalis change the colour into a yellowish green. The fluid from the larvæ of two other species of cimbex, feeding on birch leaves, gave the same results.

C. S.

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**Extracts of Meat from a Physiological Point of View.** By P. MÜLLER (*Moniteur Scientif.*, 1871, 611—626).

THIS memoir is, as the title indicates, mainly of physiological interest, and is intended to establish these propositions: that meat extracts are not aliments; that in small doses they act as stimulants by reason of the potash-salts which they contain; and that in large doses they have a toxic action, this action being also due to potash-salts.

T. S.

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**Chemistry of Vegetable Physiology and Agriculture.**

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**Origin of the Carbon fixed by Plants.** By L. CAILLETET (*Compt. rend.*, lxxiii, 1476).

WHEN the stem and leaves of a green plant are enclosed by a white glass vessel, and supplied by a gentle current of air deprived of its carbonic acid, the leaves turn yellow and fall off, and the plant soon dies. This result takes place, although the plant may be surrounded with rich soil, fully exposed to the light, and watered with rain water. If, however, when the plant appears to be perishing, the purified air be passed through a weak solution of carbonic acid, new leaves are developed, and the plant resumes its former appearance.

Carbonic acid in solution, as well as that produced by decomposition of manure in contact with the roots, is absolutely insufficient to sustain the life of chlorophyll plants. All the carbon fixed by these vegetables proceeds from the carbonic acid of the atmosphere, which, being absorbed by the green organs, is decomposed and transformed into organised products under the influence of light.

J. B.

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**On the Behaviour of Chlorophyll to Light.** By E. LOMMEL (*Pogg. Ann.*, cxliii, 568—585).

IN the spectrum of light transmitted through a concentrated solution of chlorophyll, all the light is absorbed, except the least refrangible red, near the line B. On gradually diluting the solution, the green first makes its appearance, then the yellow, the orange, and part of the red, forming a very characteristic spectrum—I, a broad dark band close behind B, which is darkest between B and C; II, a second absorption-band in the orange between C and D; III, a third a little behind D;

and a fourth, IV, in the green close before E. Of these bands, I is by far the darkest, making its appearance even in very dilute solutions, whilst II, III, and IV gradually diminish in intensity. The whole of the more refrangible portion of the spectrum is also absorbed, but just before G the absorption is seen to be somewhat weaker, increasing again behind G, this being the interval between the two broad ill-defined bands in the blue and violet which Hagenbach (Pogg. Ann., cxli, 245) designates as VI and VII, whilst V is a band in the green behind *b*, which does not appear in fresh solutions of leaf-green, but only in those which have been modified by the action of light.

The *fluorescence* of chlorophyll is also very characteristic. When a solution of the substance is illuminated by a pure sun spectrum, the red fluorescent light will be seen over all the spectrum with the exception of the extreme red, beginning just before B, and extending with varying intensity to the ultra violet. In this spectrum seven bright bands may be observed—the first between B and C; the second between C and D, rather nearer to D; the third close behind D; the fourth immediately before E; the fifth, which is seen only in the modified solution behind *b*; and the sixth and seventh, beginning behind F, cover the rest of the spectrum. Of these, the first, between B and C, and the last, VI and VII, are the brightest. It will be seen that these bright fluorescent bands correspond both in position and intensity with the dark absorption-bands, showing the intimate relation between fluorescence and absorption. The red fluorescent light, when concentrated and examined spectrally, is found to consist entirely of red rays corresponding in refrangibility with those between B and C.

The absorption spectrum of solid chlorophyll has a great resemblance to that of the solution, a thick layer of green leaves absorbing all the rays of the spectrum from B to the violet end. A thinner layer shows a dark band beginning before B and reaching to behind C; it transmits the red, orange, yellow, and green light between C and E; just behind E the spectrum begins to darken, and from the middle point between F and G it is opaque. The dark bands II, III, and IV of the solution do not appear, powerful absorption only being found in the violet, and in the red between B and C. As solid chlorophyll does not exhibit the phenomenon of fluorescence, the red rays between B and C can only be indirectly absorbed.

The rays which act most powerfully in promoting assimilation are evidently those which are most readily absorbed, and have the greatest “mechanical intensity.”

For measuring the mechanical intensity of the sun's rays, the “physiological intensity,” that is, the brightness of the light, is of no value; and the same may be said of its “chemical intensity,” that is, the action it produces on silver salts. Mechanical intensity must be determined by means of a substance capable of absorbing all the rays equally, such as lampblack, so that by means of a linear thermopile covered with it, and a galvanometer, the mechanical intensity of the various portions of the spectrum may be determined by observing the amount of heat generated, and this independently of any specific absorptive power. As it is well known that the maximum of heat is in the



ultra red of the spectrum, and that it gradually diminishes towards the violet end, the most active rays in effecting assimilation in plants will be those between B and C; the blue and violet, on the contrary, although they are readily absorbed, produce but little effect, since their mechanical intensity is but small. The extreme red also has no action, notwithstanding its great mechanical intensity, as it is not absorbed; the same may be said of the yellow, orange, and green.

The various researches on the assimilation of plants bear out this view, but unfortunately they cannot be readily compared with one another, as the mechanical intensity of the light employed has been left undetermined. In the recent researches of Prof. Sachs,\* a leaf was exposed in an atmosphere of carbonic acid to the light of the sun, transmitted through various coloured solutions, the amount decomposed by insolation being ascertained by determining the residual carbonic acid. The following were the results obtained:—

Absorbing fluid.	Decomposed carbonic acid.
Water .....	100
Potassium chromate .....	88·6
Ammonia copper oxide .....	7·6
Orsellin .....	53·0
Aniline violet .....	38·9
Aniline red .....	32·1
Chlorophyll .....	15·9

It will be seen that the potassium chromate which transmitted the red between B and C gave the highest result. Good results were likewise obtained with the other red liquids, but chlorophyll and the ammonia-copper oxide, which cut off the red end of the spectrum, gave very low results. Sachs, however, incorrectly infers from these experiments that the yellow rays, which are the brightest in the spectrum, have also the greatest effect in promoting assimilation; but an inspection of the above table will show that this cannot be the case. Chlorophyll transmits the yellow light extremely well, whilst orsellin, aniline violet, and aniline red are opaque to it.

Although the red rays between B and C are the most active in causing the elimination of oxygen, it must not be imagined that a plant illuminated by them alone would thrive, for other constituents require light of different refrangibilities; protoplasm, for example, absorbing the violet rays. As the solid chlorophyll in the plant has no fluorescence, the opinion that the fluorescent properties of chlorophyll are useful in converting the comparatively inactive highly refrangible rays into the less refrangible active rays falls to the ground.

C. E. G.

### The Action of Light on Chlorophyll. By E. GERLAND (Pogg. Ann. cxliii, 585—610).

ALTHOUGH chlorophyll became the subject of various researches as soon as its importance in plant-life was fully recognised, the changes

\* Work of the Bot. Inst. of Würzburg, by Dr. J. Sachs, Part I. The action of coloured light in decomposing the carbonic acid of plants. Leipzig, 1871.

which it undergoes when exposed to light have hitherto been but little studied.

I.—It has long been known that a chlorophyll solution when exposed to light becomes changed in colour, and Stokes (Pogg. Ann., Erg. iv, 128) has found that this chlorophyll, precipitated from its alcoholic solution and again dissolved in ether, undergoes no further change when exposed to diffused light. This *modified* chlorophyll has a somewhat different spectrum from the fresh, the dark band III (Pogg. Ann., cxli, 266, and cxliii, 231) being lighter and displaced towards the more refrangible end of the spectrum, whilst a bright band exists between *b* and F, so that, in the modified chlorophyll, there are five dark bands between *a* and F, whilst in the fresh there are only four. In order to investigate this change more thoroughly, the absorption-spectra of various chlorophyll solutions were examined in the manner previously described by Rauwenhoff and the author, both prior to exposure, and at intervals during insolation.

1. *Alcoholic Solution of fresh Chlorophyll*.—This solution, which was simply an alcoholic extract of the leaves of *Urtica dioica*, previously boiled in water, showed the band III very distinctly and stronger than IV, which was very feeble. Exposed to sunlight it had perceptibly changed colour in five minutes, in ten it was olive green, in fifteen brown, and after the lapse of an hour it had become bright yellow, and no longer showed any signs of fluorescence. During this change the absorption-bands gradually became more indistinct, and disappeared in their order, I being the most stable; eight days insolation rendered it almost colourless in thin layers, but in thicker ones it appeared of a brownish yellow, and gave the same absorption spectrum as Filhol's yellow (Ann. Chim. Phys. [4], xiv). The same change took place in diffused light, but more slowly. The alcoholic solution of the leaves of *Urtica dioica* which had been previously treated with cold water, as also that prepared from *Sambucus nigra*, which had been boiled with water, gave the same spectrum, although the solutions differed slightly in colour.

2. *Alcoholic Solution of half-modified Chlorophyll*.—A solution which had been prepared from the leaves of *Brassica oleracea* in December, 1870, and exposed to a diffused light for about two months, gave a spectrum between that of fresh and modified chlorophyll. Its colour was brownish-green, and gave the dark band III but weakly, whilst V was scarcely distinguishable. Exposed to insolation, it gradually faded, but more slowly than the freshly prepared solution; for even after being exposed to sunshine for eight hours, and to daylight during several days, it still showed all the dark bands except III, but much more faintly than before. After another eight hours' sunshine and several days more of diffused light, I was still very faintly visible, and even when it was submitted to insolation for six hours more, a considerable thickness of the solution showed traces of the band I. A solution, which had been made by Rauwenhoff in 1865, and since kept in the dark, gave the same results.

3. *Completely modified Chlorophyll*.—An ethereal solution of modified chlorophyll becomes faded, but very slowly; after 42 hours' insolation, a stratum of the solution 15 mm. thick had the same colour as one of



the original solution 2·5 mm. thick, but all the bands were visible, and even after forty days' exposure to light, I was still faintly visible, and the solution distinctly fluorescent. An alcoholic solution behaved in the same way, but the change took place much more rapidly.

4. *Ethereal Solution of Fresh Chlorophyll*.—This was obtained from *Urtica dioica* in a similar manner to the alcoholic solution, and had the same spectrum but the bands, with the exception of I, being darker rendered it more characteristic. Exposed to the sun's rays, it became faded much more slowly than the corresponding alcoholic solution, being only slightly changed, after one and a-half hour's action; and although it then showed the bright band of modified chlorophyll, the dark band III was not displaced. The latter, however, was much broader, so that it occupied the space covered by the dark bands in both modified and fresh chlorophyll. On continuing the insolation, a more rapid change took place, the colour became browner, and after a time III disappeared, giving the spectrum of the incompletely modified chlorophyll.

5. *Solid Chlorophyll*, precipitated on paper from its alcoholic or ethereal solution, fades completely and rapidly in sunlight, but more slowly in diffused day light. The chlorophyll cells in a leaf of *Sambucus nigra*, from which the epidermis had been removed, became colourless on exposure to sunlight.

6. *Ethereal Solution of Frémy's Phylloxanthin* (*Compt. rend.*, 1860).—This, when submitted to insolation, behaved precisely like modified chlorophyll.

7. *Alcoholic Solution of Filhol's Green* (*Ann. Chim. Phys.* [4], xiv).—This, by long continued insolation, became completely faded, showing no trace of absorption or fluorescence. When the solution was evaporated, it left a colourless waxy substance which frothed with sulphuric acid, but not with hydrochloric acid or nitric acid. This green behaved in the same manner whether prepared from dried or from fresh leaves.

As the chlorophyll in plants is evolved from a yellow colouring substance, so does it again become yellow on fading, and therefore it is possible that the yellow residue which is left in autumn leaves, may be faded chlorophyll.

II.—Hitherto there has been no distinction made between modified and faded chlorophyll, so that the theories respecting its fading and decolorisation are very contradictory.

Jodin (*Compt. rend.*, lix, 859) found that an alcoholic solution of chlorophyll exposed to sunlight absorbed oxygen, whilst Timiriaseff (*Botan. Zeit.*, xxvii, 885), on the contrary, states the fading to be a process of reduction. The latter appears to be borne out by the observation made by Rauwenhoff and the author, that in one instance there was an odour of aldehyde in the alcoholic solution from which modified chlorophyll had been precipitated. Although the author has since frequently repeated this experiment, he has not again been able to detect aldehyde, and has therefore endeavoured to settle this point by insulating two exactly similar test-tubes of chlorophyll solution through one of which oxygen or ozonified air was past, but it faded with nearly equal rapidity in both cases. As neither the ether nor the alcohol employed as solvents undergoes any change when the chloro-



phyll fades, if it fades through oxidation, the oxygen must be taken from the air or from that dissolved in the alcohol. When strongly ozonified air was passed up into a boiled alcoholic solution of chlorophyll standing over mercury, a small quantity of gas was at first absorbed, and the solution became somewhat darker, but after that no further absorption took place. The presence of oxygen is necessary, however, to start the action, for both the alcoholic and ethereal solutions which had been sealed up in glass tubes from which the air had been expelled by boiling the liquid, could be exposed to the sun's rays without undergoing any change, but directly the air was admitted and they were submitted to insolation, the colour of the solutions began to fade. It would seem, therefore, that both oxygen and light are necessary to produce chemical change in chlorophyll, so that when the solution is exposed to light and air, oxygen first combines with the chlorophyll which begins to be modified, and then, if the insolation be continued, it fades, but if exposed only to a feeble light, the oxidation at first set up continues and the chlorophyll becomes modified.

III.—As the dark bands disappear when chlorophyll fades and becomes decolorised, the theory of Pfeffer (*Bot. Inst. Würzb.*, i, 50) that the rays absorbed by the solution are changed into heat, becomes inadmissible, it being much more probable that they produce chemical action. To test the accuracy of this view, a chlorophyll solution was first submitted to the action of the rays of different parts of the spectrum, but no satisfactory result was obtained. A repetition was then made of the experiment of Sachs (*Handbuch. Exper. Phys. Pflanz.*), who had observed that when a chlorophyll solution was exposed to light which had previously passed through another stratum of the same fluid, it did not begin to fade until the other was much changed. The author having arranged an apparatus for this purpose, found that when the protected or test solution began to fade, the band I in the spectrum of the protecting solution had become foggy and indistinct, whilst the dark bands II and III had completely vanished. As therefore light of a refrangibility corresponding to the dark bands II, III, IV and V had produced no effect upon the test-solution, it could only be the rays of the same refrangibility as I and the blue, which caused the solution to fade. When the protecting solution was a concentrated ethereal solution of modified chlorophyll, no change took place in the test solution even after several days' insolation. On examining this protecting solution spectroscopically, the band I was seen to be quite black, whilst the red and yellow rays on each side of it were freely transmitted. From the results of this series of experiments, it seemed that the obscure heat-rays take no part in causing the chlorophyll to fade, and in order to confirm this, a solution of chlorophyll was exposed to bright sunshine from which the heat-rays had been excluded by passing it through a stratum of water 130 mm. thick. The colour of the solution, however, faded as quickly as that of one exposed to the direct rays of the sun. In order to ascertain whether it was the red rays corresponding to the band I or the blue and violet from G to H, or both of these which caused the change, solutions of chlorophyll were exposed behind red glasses (coloured with copper oxide), and an ammoniacal solution of copper sulphate respectively. The colour of the solution slowly

faded in both cases, but on exposing the solution to the light transmitted through green glasses (consisting of the green and a few yellow and blue rays), no change took place, from which the author concludes that chlorophyll fades only when exposed to light of the same refrangibility as that which is absorbed by it.

IV.—Lastly, it seems likely that the examination of the absorption-spectrum of leaves would tend to solve the question as to whether there is any connection between the fading of chlorophyll and the assimilation of plants. Müller (*Pogg. Ann.*, cxlii, 615) on examining several species of green leaves by direct sunlight, was unable to distinguish any dark bands in the spectrum. The author, therefore, repeated the examination with light of more moderate intensity, when the band I was in all cases found to be present, and with most species of leaves the bands II, III, and IV, although they presented certain peculiarities. Notably the leaves of *Ficus elastica* gave III much broader. Melde (*Pogg. Ann.*, cxxvi, 277) has already shown that the turbidity of the solution may cause an alteration in its absorption spectrum, and as it was possible that the peculiarities above mentioned might arise from the layer of chlorophyll not being homogeneous, an experiment was made to ascertain whether this was the case. The spectra of a turbid chlorophyll solution, formed by mixing an ethereal solution with soap-water, was examined, as also an alcoholic solution, to which a large quantity of soap had been added, but the results were unsatisfactory.

The researches which have hitherto been made, and especially those of Draper (*Phil. Mag.*, xxiii, 161, and xxv, 169), Sachs (*Bot. Zeit.*, 1864, 363), and Pfeffer (*loc. cit.* 459), have shown that red and yellow light is that which is most active in promoting assimilation, but the author does not consider the theory of Pfeffer well established, that the physiological intensity of the light may be expressed by the curve which passes through the extremities of the ordinates drawn to a linear spectrum, the length of the ordinates in any colour being proportional to the amount of carbonic acid decomposed by rays of that colour, especially as the light employed by him in his experiments was not achromatic. The author arrives at the conclusion that the rays of light which are absorbed by the chlorophyll are those which most powerfully promote assimilation.

C. E. G.

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**The Action of Atmospheric Nitrogen in Vegetation.** By  
P. P. DEHERAIN (*Compt. rend.*, lxxiii, 1352—1355).

THE author believes that the sources of the nitrogen of the soil, at present recognised, are insufficient to account for the amount of nitrogen which soils contain; he endeavours to prove that the free nitrogen of the atmosphere is brought into combination during the oxidation of the organic matter of the soil. The following experiments he considers justify this conclusion. If 15 grams of glucose are mixed with 15 c.c. of water, and the same quantity of ordinary ammonia, and placed in a flask with 200 c.c. of equal volumes nitrogen and oxygen, and the flask then closed and heated for 100 hours in the water-bath, the whole of the



oxygen is absorbed, and also (on an average of 20 experiments) 5.9 per cent. of the nitrogen, while no carbonic acid gas is produced. When the nitrogenous glucose (*glucose azoté*) of P. Thénard is treated in the same manner, the absorption of nitrogen averages 15.4 per cent. Humic acid, mixed with solution of potash, and acting on atmospheric air, absorbs 7.2 per cent. of the nitrogen, and humus from old wood, with potash, absorbs 3.6 per cent. The author has not yet determined the nature of the nitrogenous compounds formed in these reactions.

R. W.

**On the Action of Potassium in Vegetation.** By F. NOBBE, J. SCHROEDER, and R. ERDMANN (Versuchs-Stationen Organ, xiii, 321—423).

THE authors proposed to ascertain by water-culture experiments—I. How a plant behaves in a solution destitute of potassium, but in other respects complete. II. What influence have different combinations of potassium on the plant. III. Whether sodium or lithium can replace potassium in its physiological action. A large number of experiments were made with Japanese buckwheat, and a smaller number with summer-rye. Seven solutions were employed; the following formulæ show the proportions of the salts contained in each:—

I.	II.	III.	IV.	V.	VI.	VII.
8KCl.	—	8KNO <sub>3</sub> .	4K <sub>2</sub> SO <sub>4</sub> .	10KH <sub>2</sub> PO <sub>4</sub> .	8NaCl.	8LiCl.
4CaN <sub>2</sub> O <sub>6</sub> .	4CaN <sub>2</sub> O <sub>6</sub> .	4CaCl <sub>2</sub> .	CaCl <sub>2</sub> .	CaCl <sub>2</sub> .	4CaN <sub>2</sub> O <sub>6</sub> .	4CaN <sub>2</sub> O <sub>6</sub> .
—	—	—	3CaN <sub>2</sub> O <sub>6</sub> .	3CaN <sub>2</sub> O <sub>6</sub> .	—	—
MgSO <sub>4</sub> .	MgSO <sub>4</sub> .	MgSO <sub>4</sub> .	MgSO <sub>4</sub> .	MgSO <sub>4</sub> .	MgSO <sub>4</sub> .	MgSO <sub>4</sub> .
<i>x</i> KH <sub>2</sub> PO <sub>4</sub> .	<i>n</i> HCl.	<i>m</i> H <sub>3</sub> PO <sub>4</sub> .	<i>m</i> H <sub>3</sub> PO <sub>4</sub> .	—	<i>r</i> NaH <sub>2</sub> PO <sub>4</sub> .	<i>m</i> H <sub>3</sub> PO <sub>4</sub> .
<i>y</i> FePO <sub>4</sub> .	<i>y</i> FePO <sub>4</sub> .	<i>y</i> FePO <sub>4</sub> .	<i>y</i> FePO <sub>4</sub> .	<i>y</i> FePO <sub>4</sub> .	<i>y</i> FePO <sub>4</sub> .	<i>y</i> FePO <sub>4</sub> .

The buckwheat plants in solutions II, VI, and VII (without potash), grew very little; the addition of potassium chloride to individual cases of II and VI at once established active growth. The plants supplied with lithia (VII) were dead in six weeks. To investigate this injurious action of lithia, a supplementary solution, containing both potassium and lithium chloride, was employed; in this solution decided growth was obtained, but of a very slender and unhealthy character.

The buckwheat in solutions I, III, IV, and V (to which various salts of potassium had been supplied), exhibited active growth. At first the growth was alike in all; the plants, however, in I and III soon showed in advance, and were the only ones that finally perfected seed. The plants in IV and V were dwarf in character, the leaves thick fleshed, and curling inwards; only one plant (in series V) blossomed. In a new series of experiments, started later in the season, the plants in solutions IV and V did much better; the advantage, however, as before, was with solution I.



An elaborate microscopic investigation was made on various parts of the buckwheat plants at different stages of their growth, with the view of discovering the effect of potash on the formation of starch. The small plants grown without potash contained decidedly less starch than plants of similar age receiving potash. Plants of series II showed an increase of starch in the chlorophyll grains of the leaves two days after the addition of potassium chloride to the solution. The dwarf plants of series IV and V showed an abnormal accumulation of starch in the leaves, causing them to swell and curl as already noticed; in the stem the amount of starch was small and irregularly distributed. The plants of I, and to a rather less extent III, exhibited an abundant but normal distribution of starch.

The authors remark that the "starch-sickness," from which the buckwheat suffered in IV and V, was the same malady which Nobbe had observed in a more aggravated form when buckwheat was grown without chlorine; the starch remains in the leaves where it is formed, and the development of the plant ceases.

The plants when harvested exhibited considerable differences of weight among members of the same series. The average weights in milligrams are given in the following table.

Series.	Number of Buckwheat plants harvested.	Dry substance in		Potash in 100 of dry substance.
		Total seed.	Whole plant.	
I. Potassium chloride .....	10	1780	20295.0	2.617
III. Potassium nitrate .....	4	1370	17400.0	2.784
IV. Potassium sulphate ....	3	—	849.5	2.660
V. Potassium phosphate ....	4	—	1520.0	2.767
II. No potassium .....	17	—	67.5	.791
VI. Sodium chloride .....	8	—	117.1	.999
VIII. Lithium and Potas- sium chloride..... }	5	—	385.6	—

The seed from which the plants were grown contained 30.6 milligrams of dry substance.

The experiments with summer-rye were made at the same time, and in similar solutions. The plants grown without potash were extremely feeble; those receiving lithia were more sickly than those receiving soda, but not to the marked extent observed with buckwheat. No great difference appeared between series I, III, IV, and V, up to blooming; after this point the plants of IV produced a great number of new shoots; these formed ears which remained unfruitful. No microscopical observations were made.

The rye-grain used at starting contained 24 milligrams of dry matter. The average dry matter in the harvested produce was, in milligrams, as follows; there were great differences among plants of the same series.

Series.	Number of Rye plants harvested.	Dry substance in		Seed in 100 of dry substance.
		Total seed.	Whole plant.	
I. Potassium chloride .....	12	1669·6	5226·6	31·9
III. Potassium nitrate .....	6	1112·0	5751·7	19·5
IV. Potassium sulphate ....	6	310·6	6305·8	4·9
V. Potassium phosphate ....	6	1304·7	5455·0	23·9
II. No potassium .....	11	—	38·5	—
VI. Sodium chloride.....	6	—	47·2	—
VII. Lithium chloride.....	6	—	45·7	—

The authors conclude that without potassium the chlorophyll grains of the leaves are unable to form starch; that sodium and lithium are quite unable to replace potassium in this function, lithium being actually injurious. Further, that the form of combination under which potassium is supplied is most important, and that the chloride is the most efficacious salt.\*

R. W.

#### Influence of the Temperature of the Soil on the Development of Certain Plants. By J. BIALOLOCKI (Versuchs-Stationen Organ, xiii, 424—472).

THE plants were cultivated in glass pots, filled with sand manured with a solution of mineral salts; the pots were maintained at constant temperatures, by means of hot-water baths, or ice, as desired. The author ascertained the effect of eight soil temperatures (8°—40°) on the growth of wheat, rye, and barley, up to the first sign of a flowering stem. Every pot contained six plants of each kind. The rye plants were the earliest developed. After three weeks' growth the plants were harvested. Rye gave its maximum yield of dry matter at 20°; barley at 25°; wheat at 30°. It is well known that rye can be grown in colder climates than wheat; barley is cultivated in higher latitudes than either, by reason of its speedy growth.

A further series of experiments (B) was made on barley, with soil temperatures of 10°, 20°, 30°, and 40°. The earliest development was, throughout, in II, III, and an extra pot at atmospheric temperature. Harvest took place three months after sowing; II, III, and 1a, were then milk-ripe; I was less forward; IV had not fructified, and was decidedly unhealthy. The roots exhibited great differences. With I they were short and thick, and covered with warty knobs. With II

\* The authors assume throughout the paper that the plants actually received potassium in the form in which it was supplied to the solution; whereas the potassium in each solution must have existed in combination with all the acids present. There is no difference in elementary composition between solutions I and III, save that the latter contains less of potassium and phosphoric acid; yet all the differences in the results are attributed to the one supplying chloride, the other nitrate of potassium. Solutions IV and V should only be characterised as respectively rich in sulphates and phosphates, and poor in chlorides. See on this subject Gladstone, Phil. Trans., 1855, p. 183.—R. W.

and III they were much more branched, the maximum bulk and distribution being in III. With IV there was a fine network of root confined to the top of the pot.

In a third series of trials (C), barley was grown at the ordinary temperature for two months, till the fourth leaf was developed; the pots were then subjected to the same temperatures as in series B. For about a week no change was observed; the ill effect of the highest temperature then began to appear; there was throughout little observable difference between I, II, and Ia. The plants were reaped four months after sowing; II and III were then nearly ripe, the others less so. The character of the roots was similar to that in series B; the lower part of the roots of IV had died away. The following table shows the weight of dry substance (in grams) produced at each temperature in series B and C:—

Num-ber.	Tempe-rature.	Barley, series B.				Barley, series C.			
		Roots.	Leaves and stalks.	Ears.	Whole plant.	Roots.	Leaves, stalks, chaff.	Corn.	Whole plant.
I ....	10°	1·068	5·407	1·164	7·639	·740	3·883	2·707	7·330
II. ...	20°	·878	4·528	2·816	8·222	·838	5·132	3·180	9·150
III ..	30°	·427	1·903	1·524	3·854	·564	2·402	2·366	5·332
IV ..	40°	·155	·637	·137	·929	·234	1·776	1·463	3·473
Ia. {	of the } air }	1·221	4·711	2·210	8·142	·925	3·944	3·272	8·141

Plants will receive no apparent injury from a soil temperature of 55°, if it last but a few hours. Very young barley plants will endure 50° for 4—5 days; but after the plant has produced two leaves, it is killed by this temperature in 12—20 hours.

The temperature of the air during the experiments is recorded.

R. W.

### Influence of Light on the Germination of the Kidney-Bean.

By H. KARSTEN (Versuchs-Stationen Organ, xiii, 176—195).

THE beans selected were as uniform as possible. After weighing, they were allowed to germinate between wet blotting-paper, and the shells removed. When the roots were sufficiently developed, the beans were supported on gauze, with their roots in distilled water. One series was then exposed to direct sunlight, the roots only being shaded; the other series was kept wholly in the dark. Each bean was harvested as soon as the second leaf began to make its appearance; this occurred in 15—20 days in sunlight, and in 25—30 days in darkness. The number of beans germinated in this manner was 564.

The plants grown in the dark were of far greater length than those exposed to sunlight. The proportion of the various parts is shown in the following table; the figures represent the yield of 1,000 grams of air-dried beans, containing 745 grams of dry, shell-free matter.



		Leaves.	Stalks of first leaves.	Inter- nodes.	Roots.	Cotyle- dons.	Total plants.	Original beans.
Light	{ fresh weight ..	722·0	115·0	615·0	1038·0	1551·0	4041·0	1000
	{ dry weight ....	114·6	12·3	78·3	87·0	334·3	626·5	745
Darkness	{ fresh weight ..	134·0	293·0	2027·0	832·0	1582·0	4886·0	1000
	{ dry weight ..	22·6	19·6	174·0	62·4	277·7	556·2	745

The loss of weight in germination is seen to be greatest in the dark ; the leaves had not in this case the nutritive action which they probably exercised in sunlight.

The author made a separate chemical analysis of each part of the young plants. The composition of the dried, entire plants is compared below with that of the original beans, 1,000 grms. of air-dried beans serving as before for comparison.\*

	Composi- tion of original beans.	Grown in light.		Grown in darkness.	
		Compo- sition.	Gain or loss per cent.	Compo- sition.	Gain or loss per cent.
Crude fat .....	19·08	19·82	+ 3·92	16·00	- 16·09
Sugar .....	8·75	13·93	+ 59·16	8·42	- 3·82
Gummy matter .....	84·92	105·89	+ 24·69	78·60	- 7·45
Starch .....	146·01	74·40	- 49·04	62·21	- 57·41
Cellulose .....	17·47	57·97	+ 231·84	65·57	+ 275·34
Protein .....	185·79	160·46	- 13·63	168·69	- 9·24
Ash .....	30·17	34·85	+ 15·49	35·43	+ 17·44
Non-nitrogenous matter undetermined..... }	252·81	159·20	- 37·03	121·31	- 52·01
Total dry matter ..	745·00	626·52	- 15·90	556·23	- 25·31

The water in which the young plants grew was examined ; it contained but a trace of solid matter.

R. W.

### State of a Forest Soil before and after Liming. By T. SCHLÖSING (Compt. rend., lxxiii, 1326—1330).

THE soil in question was composed of sand, with a little clay. It was originally covered with oak underwood, and had been in this condition beyond the memory of man. A part was cleared 50 years ago, and since then regularly treated with dressings of lime, and small quantities of farmyard manure. The author found no lime in the soil or subsoil of the forest land ; while the cultivated soil contained 1·583 per cent.,

\* From the method of analysis followed, it seems probable that both starch and cellulose were under-estimated ; the large amount of undetermined matter is most likely due to this cause.—R. W.

and its subsoil '609 per cent. He removed from the soils, by displacement the matters they held in solution, operating for this purpose on 35 kilograms of each soil. The solution from the forest soil contained no nitrates; that from the cultivated soil held a large amount. The cultivated soil yielded considerably more of chlorides, sulphates, and lime than the forest soil; but less of potash, soda, and organic matter. The author speculates on the formation of calcium chloride in the limed soil, by decomposition of common salt brought by rain from the neighbouring sea; he also shows by experiments, that the addition of potassium or calcium chloride to a calcareous soil does not apparently favour the formation of nitric acid. R.W.

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**The Spring-Period of Birch and Maple.** By J. SCHROEDER  
(Versuchs-Stationen Organ, xiv, 118—146).

BIRCH and maple bleed when bored in root or trunk in spring time, before the appearance of leaves. Bleeding can first be obtained from the root, then slowly, step by step, from higher parts of the tree. Bleeding continues in the root for a short time after it has ceased in the trunk. Birch begins to bleed one week before maple, and continues bleeding about one week later, the whole period being six or seven weeks. Birch sap, obtained during bleeding, contains '34—1.92 per cent. of fruit-sugar; maple sap, 1.15—3.71 per cent. of cane-sugar. With birch the proportion of sugar in the sap at any one level diminishes very steadily as the bleeding period advances. The sugar appears to increase to a slight extent from the root upwards, but beyond a certain moderate elevation a rapid decrease takes place. The leaf-buds unfold towards the end of the bleeding period, and the richness of the sap in sugar may be easily predicted from the stage of development the buds have reached. With maple, on the contrary, buds never open till bleeding ceases. No sugar being here consumed for the production of leaf, we consequently find that the quantity in the sap does not diminish till nearly the end of the bleeding period, and that the amount of sugar is greater in the higher parts of the tree, instead of smaller, as is the case with birch. Both birch and maple contain much reserve starch in winter time. Famintzin and Borrodin have observed the annual formation and disappearance of transitory starch in birch; the author has proved by microscopical investigation, that starch diminishes in the bark and wood of maple during the development of buds; but, as yet, he fails to establish a connexion between the disappearance of starch and the formation of sugar.

Birch and maple sap contain from '007 to '034 grm. of albumin per litre, and '3 to 1.3 grms. of mineral matter. In birch the albumin increases during the first days of bleeding, and afterwards diminishes more rapidly than the sugar. The mineral matter rises considerably in amount as bleeding progresses, and suffers little decrease towards the end; the quantity is much less in the higher parts of the tree, though, curiously, the potash suffers no diminution. The results with maple sap were fewer and less distinct. Birch and maple sap also contain malic acid; in birch sap from '23 to '60 grm. per litre was found; the



amount rose towards the middle of the bleeding period, and then decreased. R. W.

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**Pyrocatechin, an Element of Living Plants.** By E. v. GORUP-BESANEZ (Deut. Chem. Ges. Ber., iv, 905).

DURING the examination of the green leaves of the Virginia Creeper, *Ampelopsis Hederacea*, the author obtained a precipitate with lead acetate, which, after decomposition by hydrogen sulphide and neutralisation with milk of lime, yielded a liquid, which rapidly darkened in colour, and had the characteristics of a solution of pyrocatechin in lime-water. From leaves gathered in September a body was isolated (in too small quantity for further investigation), which was soluble in water, alcohol, and ether; its aqueous solution was precipitated by lead acetate, and gave, with dilute ferric chloride, an emerald-green colour, becoming pure violet on the addition of a drop of dilute sodium-hydrogen carbonate; it caused the reduction of copper and silver solutions on warming.

Tartaric acid, potassium-hydrogen tartrate, calcium tartrate, gum, and a fermentable sugar resembling inverted sugar, were also found to be present. C. R. A. W.

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**Contributions to the Chemical History of the Roman Chamomile.** By CAMBOULISES (J. Pharm. Chim. [4], 337—341).

PATTONE has already published an analysis of the flowers of the common chamomile, *Anthemis arvensis*, from which it appears that it contains a peculiar acid, anthemis acid, and a new alkaloid, anthemine.

The flowers of the Roman chamomile have not yet been analysed, although the extract has been studied by several chemists, among others by Bornträger and Gerhardt. 100 grams of the flowers treated with ether furnished an extract weighing 6.344 grams. This, on boiling with water, yielded 0.738 gram soluble matter. The insoluble residue consisted of a waxy looking substance and a small quantity of chlorophyll. The aqueous solution, at first perfectly clear, became turbid on cooling, and deposited a yellow granular substance. This yellow body dissolved completely in alcohol, and gave the following reactions:—A bottle-green precipitate with ferric chloride; with neutral lead acetate and with ammonia, yellow precipitates. It was impure quercitrin. The clear portion of the aqueous solution of the ethereal extract treated with magnesium sulphate and with ammonia gave a yellowish brown precipitate consisting principally of impure magnesium-ammonium phosphate. The aqueous solution, evaporated to dryness and shaken up with ether, gave on spontaneous evaporation a residue seen under the microscope to consist of prismatic needles, exceedingly bitter in taste, and reacting strongly on blue litmus. Its solution gave no reaction with ferric chloride; neutral lead acetate gave a very slight precipitate, appearing only after some time; calcium and barium chlorides and silver nitrate gave no precipitate. On heating, the crystals are decomposed without volatilising. It would appear from these observations that the flowers of the Roman chamomile contain a peculiar acid, probably identical with that found by Pattone in the flowers of common



chamomile. The author's observations, however, are necessarily incomplete, as he has only been able to obtain a minute quantity of the substance.

After exhausting the flowers with ether, the alcoholic extract had no longer a bitter taste, but contained a yellowish fatty substance.

The flowers of Roman chamomile treated with distilled water gave a notable quantity of glucose. The amount obtained varied with the method of analysis—by Fehling's solution, 23.498 grams; by the fermentation method, 14.890 grams per 100 grams of the flowers. It would appear that the flowers of the Roman chamomile contain other substances than glucose, which reduce Fehling's solution. 100 grams of flowers yielded 6 grams of ash, consisting of—

Soluble matter ..	{	Potassium sulphate .....	0.8103
		Potassium chloride .....	1.1629
		Potassium carbonate ....	1.1907
		Alkaline phosphate .....	0.0111
			<hr/>
			3.1750
Insoluble matter..	{	Silica.....	0.3976
		Calcium phosphate .....	1.6894
		Magnesium phosphate....	0.1593
		Calcium carbonate .....	0.5798
			<hr/>
			2.8252

The author has repeated the process of Pattone without having been able to detect in the flowers of the Roman chamomile the peculiar alkalioid discovered by the latter chemist in the common chamomile.

T. E. T.

**Allyl Sulphocyanate, a Constituent of the Root of Mignonette** (*Reseda odorata*). By A. VOLLRATH (Arch. Pharm. [2], cxlviii, 156).

THE root of this plant has a pungent taste, and emits, when cut up, an unmistakable odour of horse-radish. When macerated with hot water and distilled, it yields an oily distillate, which, when mixed with silver nitrate, turns brown, and forms, after some time, a precipitate of silver sulphide. The same distillate boiled with baryta-water yields barium carbonate, barium sulphide, and sinapoline. A quantity of the distillate was treated for some days with excess of ammonia solution, and then evaporated to dryness. A yellow crystalline mass was obtained, which was decolorised by boiling with water and animal charcoal. The filtrate from the animal charcoal, &c., on evaporation furnished a small quantity of a white, shining, crystalline substance, which exhibited the reactions characteristic of thiosinamine, and under the microscope the rhombic prisms of that body.

W. S.

*Sewage as a Fertiliser of Land, and Land as a Purifier of Sewage.*  
By J. B. DENTON (Chem. News, xxv, 6, 15).

## Analytical Chemistry.

### Estimation of Nitrous Acid in Nitrous Sulphuric Acid.

G. E. DAVIES (Chem. News, xxiv, 257—259; xxv, 25) has investigated two of the best known methods for this purpose, viz., the “chloride of lime” and the “permanganate” processes. The results of the former are apt to be vitiated to some extent by loss of chlorine, to guard against which, the author proceeds as follows: Into a stoppered bottle having a capacity of 1750 cub. cent., he introduces a litre of water, and then 10 cub. cent. of a chloride of lime solution containing 7 grams of chlorine. The nitrous vitriol is then poured in, the stopper instantly replaced, and the bottle repeatedly agitated till there is no smell of chlorine; a few drops of indigo sulphate are then added, and if the solution keeps its blue colour, the operation is ended.

The sources of error in the permanganate process appear to arise—1stly. From the fact that the organic matter which colours the brown oil of vitriol of commerce is readily acted upon by the permanganate, and is found to vary very much in amount. 2ndly. Some vitriols contain more arsenious compounds than others; these would of course act equally upon both “chloride” and “permanganate” solutions. 3rdly. The large excess of vitriol interferes with the accuracy of the reaction. The dilution of the nitrous acid also affects the results. The author believes that these sources of error may be reduced to a minimum by adding the nitrous vitriol to the permanganate solution.

A series of experiments made by these two methods on the same samples of vitriol gave the following average percentages:—

- |  |                |   |               |
|--|----------------|---|---------------|
| 1. By chloride of lime process . . . . | 0.75 per cent. | } | of $N_2O_3$ . |
| 2. By permanganate process . . . .     | 0.63 „         |   |               |

The author likewise gives the results of the estimation of the nitrous acid in five different samples of nitrous vitriol by three processes: 1st, the chloride of lime; 2nd, the process by which the  $N_2O_3$  in 10 c.c. of the vitriol is estimated by addition of decinormal permanganate (the  $\alpha$  permanganate process); 3rdly, the  $\beta$  permanganate process, in which the nitrous vitriol is added to 50 c.c. decinormal permanganate until decoloration takes place:—

	Percentage of $N_2O_3$ .				
	I.	II.	III.	IV.	V.
Chloride of lime. . .	1.184	1.119	1.609	2.239	0.669
$\alpha$ Permanganate ..	1.148	1.064	1.501	2.128	0.570
$\beta$ Permanganate ..	1.158	1.117	1.418	2.159	0.673

The chloride of lime process appears to be the best for general use: but when the proportion of nitrous acid present is very small, not exceeding 0.02 to 0.2 in 100 parts of the sulphuric acid, the permanganate process is to be preferred, and under these circumstances it is very easily and quickly performed.

According to W. CROWDER (Chem. News, xxiv, 237 and 249), Hart's urea process for estimating the nitrous acid in vitriol from the Gay-Lussac column and denitrators is not satisfactory; but he has contrived a modification of it, which appears to give trustworthy results. The decomposition of urea by nitrous acid takes place, as is well known, according to the equation  $\text{CN}_2\text{H}_4\text{O} + \text{N}_2\text{O}_3 = \text{CO}_2 + 4\text{N} + 2\text{H}_2\text{O}$ . The  $\text{CO}_2$  and N escape with effervescence, and by using an ordinary carbonic acid apparatus (the Geissler's instrument, slightly modified, was used by the author), the loss in weight is ascertained, and the amount of nitrous acid ( $\text{N}_2\text{O}_3$ ) may be calculated by the proportion—

$$\frac{\text{CO}_2 + 4\text{N}}{100} : \frac{\text{N}_2\text{O}_3}{76} = \text{quantity of CO}_2 + \text{N found} : x,$$

which gives  $x = \frac{76}{100} \times \text{quantity of CO}_2 + \text{N found}$ .

By comparing this process with one dependent on the oxidation of nitrous acid to nitrogen tetroxide or nitric acid—as by dropping the vitriol to be tested into a standard permanganate solution of known strength—it was found that the results obtained by the latter method were about one-third less than those obtained by the urea process. The reason of this the author was unable to discover; but by taking a vitriol containing a known quantity of  $\text{N}_2\text{O}_3$  as determined by the "urea" process, and standardising the permanganate by that quantity, results were obtained perfectly agreeing with the quantity of  $\text{N}_2\text{O}_3$  in other samples, as determined by the urea process.

The original paper contains tabulated results of a series of experiments in illustration.

W. S.

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**The Separation and Estimation of several Metals by the Voltaic Current.** By LECOQ DE BOISBAUDRAN (Compt. rend., lxxiii, 1922).

By employing an electric current of suitable intensity, it is possible to separate directly the more easily reducible metals from those which are less so, and to obtain in this manner two distinct groups; the first comprising iron, nickel, cobalt, and zinc; the second, all the other metals capable of reduction, the latter group also representing those metals which are precipitable by a plate of zinc.

In the electrolytic separation of two metals (copper and cadmium for example), in which the respective reducibility differs but slightly, it is found practically advantageous to employ a current somewhat stronger than would be necessary, supposing it were intended to avoid the precipitation of the less reducible metal. In this way a deposit is in the first instance obtained, containing the whole of the more reducible metal, and also a small quantity of the other metal; the solution is then poured off, replaced by a liquor free from metallic salts, and the direction of the current reversed for a short time. As soon as the deposited metals have passed into solution the original direction of the current is re-established. The less reducible metal, being now only in



very small proportion, remains entirely in solution, while the metal which is more easily reduced is deposited perfectly pure. It is sometimes, though not often, necessary to repeat this operation.

When a solution of cobalt, nickel, or zinc is reduced by galvanic influence, it is advisable to supersaturate the solution with ammonia to avoid the deposition of oxide. It is found impossible to estimate iron correctly by the above method, owing to the great tendency of the metal to form peroxide.

J. W.

### The Separation of Potassium and Sodium. By TH. SCHLÖSING (Compt. rend., lxxiii, 1269—1273).

THE use of perchloric acid as a reagent for the estimation of potassium, has, at the present day, almost fallen into disuse, partly on account of the difficulty of preparing the acid, except through the intervention of a potassium salt, and partly because the numerical results of test analyses have never been published, whereby the accuracy of the method has been allowed to remain unproved. The author endeavours to show that the former difficulty may be overcome by the use of ammonium perchlorate, and that the method is in itself deserving of confidence.

Ammonium perchlorate is prepared by boiling a concentrated solution of sodium perchlorate with a saturated solution of sal ammoniac; double decomposition takes place, and the ammonium salt is deposited on cooling in fine crystals. The solution of this salt, when boiled with dilute nitrohydrochloric acid, is instantly resolved into a mixture of perchloric, nitric, and hydrochloric acids, and upon this reaction its employment in analysis depends, inasmuch as, owing to the stability of perchloric acid it decomposes the saline combinations of nitric and hydrochloric acids, transforming the bases into perchlorates.

The separation of potash and soda is conducted in the following manner. The solution of these bases having been concentrated in a tared platinum capsule, is mixed with the solution of perchloric acid, prepared as above mentioned. The whole is then evaporated to dryness, or until white fumes begin to appear, which is an evidence that the perchloric acid is in excess, and that the transformation of the salts is complete. The potassium perchlorate is washed several times with alcohol, dissolved in a small quantity of water to separate a little adhering soda-salt, the solution evaporated to dryness, and the residue again washed with alcohol. The potassium salt is then perfectly pure, and may be dried at 250° C. and weighed. The alcoholic solution of sodium perchlorate is evaporated with addition of sulphuric acid, and the sodium weighed in the form of sulphate. By the above process the author has obtained the following results:—

Quantity used.	Found.	Potass. chloride.
Potass. chloride.... 0.6432	Potass. perchlorate .. 1.1939	= 0.6432
Sodium    ,,     .... 0.3855		Sodium chloride.
	Sodium sulphate .... 0.4678	= 0.3854

Potass. chloride....	0.0358	Potass. perchlorate ..	0.064	Potass. chloride. =0.0345
Sodium ,, ....	1.2967	Sodium sulphate ....	1.5705	Sodium chloride. =1.294
Potass. chloride....	0.7772	Potass. perchlorate ..	1.143	Potass. chloride. =0.777
Sodium ,, ....	0.0023	Sodium sulphate ....	0.0029	Sodium chloride. =0.0023

The accompanying experiment shows that the estimation of potassium is not affected by the presence, in the solution, of barium, calcium, or magnesium salts.

Quantity operated upon—

Potassium chloride .....	0.0835	gram.
Magnesium sulphate .....	0.574	„
Sodium chloride .....	1.298	„
Calcium chloride .....	0.233	„

After the elimination of the sulphuric acid by barium chloride, and conversion of the bases into perchlorates, there was found—

Potassium chloride .....	0.1531	Potass. chloride. = 0.0824
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J. W.

### Estimation of Antimony, and Separation of Antimony from other Metals. By HUGO TAMM (Chem. News, xxiv, 207, and 221—223),

WHEN a neutral and concentrated solution of antimonious chloride is mixed with a slight excess of gallic acid, the whole of the antimony is separated as insoluble antimonious gallate. This reaction the author proposes to utilize for the estimation of antimony, and for the separation of antimony from tin, arsenic, and other metals.

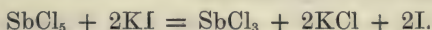
The above mentioned combination of antimony with gallic acid is insoluble in a neutral or slightly acidulated liquor, but dissolves readily in more concentrated solutions of hydrochloric acid; it is necessary, therefore, for the success of the analysis, that the solution be concentrated by evaporation, and any large excess of acid volatilized. The precipitate is somewhat bulky, but settles rapidly. It cannot, however, be washed on a filter, since it invariably passes through the filter as soon as the acidulated mother-liquor has been washed away; the mixed mode of decantation and filtration must, therefore, be resorted to, which in this particular instance presents neither inconvenience nor difficulty.

Antimonious gallate dried at 100° C. has the composition  $\text{Sb}_2\text{O}_3(\text{C}_7\text{H}_2\text{O}_3)_2 + 3\text{H}_2\text{O}$ , and contains 40.85 per cent. of metallic antimony. It is exceedingly hygroscopic.

The author does not insist that the antimony shall be weighed in the form of antimonious gallate, although the composition of the precipitate

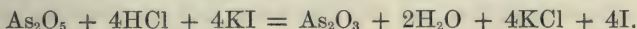
is perfectly definite; it may, if preferred, be dissolved in hydrochloric acid, and the antimony precipitated by sulphuretted hydrogen in the usual way.

Solutions of antimonious chloride are unfit for the estimation of this metal by gallic acid: they must, therefore, before precipitation, be reduced to the state of antimonious chloride. This reduction is readily effected by mixing the slightly acidulated solution of antimonious chloride with a solution of potassium iodide, when the following reaction ensues—



The iodine and excess of acid having been removed by evaporation, the solution is ready to be precipitated by gallic acid.

*Separation of Antimony from Arsenic.*—Potassium iodide, which in presence of hydrochloric acid reduces antimonious chloride to the state of antimonious chloride, with evolution of iodine, reacts in a similar manner upon arsenic acid, which it reduces to arsenious acid—



This reaction greatly facilitates the separation of the two metals. The antimony is estimated by gallic acid in the manner already described, and the arsenic precipitated subsequently by sulphuretted hydrogen.

*Separation of Antimony from Tin.*—Potassium iodide has no reducing effect upon stannous chloride, but when an excess of iodide is introduced into the solution a double decomposition takes place, and the liquor consists of a hydrochloric acid solution of stannous iodide. Experience has proved that gallic acid separates antimony from stannous iodide much more readily than from the perchloride of the same metal. If the quantity of potassium iodide employed has been properly adjusted, the antimonious gallate settles very rapidly in the liquor; on the contrary, when the operation has been badly conducted, the antimonious gallate is mixed with stannous oxide, and the whole remains in suspension without subsiding. In this case the liquor should be rejected as unfit for a successful separation.

The separation of antimony from arsenic and tin is conducted in a manner similar to the separation of antimony from tin. In this instance the author is scarcely satisfied with the results he has obtained, and does not consider that he has succeeded in solving satisfactorily the difficult problem of the ready separation of a mixture of arsenic, antimony, and tin.

J. W.

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### The Analysis of Chrome Ore. By JOHN CLARK (Chem. News, xxiv, 304).

WHEN chrome ore is attacked by fusion with acid sulphate of potassium, the precipitate of chromium oxide subsequently obtained retains a portion of the alkaline salt with great persistence, and serious variations not unfrequently occur in the assaying of chrome ores, owing to the inadequate attention which is too often paid to this circumstance.



The method of operating introduced by the author in the present paper completely eliminates this source of error.

One part of the levigated ore is mixed with eight parts of a mixture of sodium hydrate and calcined magnesia, and the whole ignited strongly for one hour in a platinum crucible. The contents of the crucible are afterwards dissolved in dilute sulphuric acid, and the chromic acid estimated by the addition of double iron salt, and titration of the excess of the latter by standard dichromate. The results obtained by this method were highly satisfactory.

In commenting upon this process, Hugo Tamm remarks (*Chem. News*, xxiv, 305) that it is not well adapted for the complete analysis of chrome ore, inasmuch as magnesia is one of the constituents of this mineral, and further, that the caustic soda employed invariably contains silicic acid and alumina. He recommends the adoption of the following method.

One part of the ore is fused with 15 parts of acid sulphate of potassium, and the excess of acid is volatilised. 10 parts of nitre and 10 parts of potassium carbonate are then projected into the crucible, and the whole mass is fused and stirred. The contents of the crucible are next disintegrated with boiling water, the solution filtered, and the alkaline liquor first acidified with hydrochloric acid, then *rapidly* neutralised with ammonia and ammonium carbonate. By this means silica, alumina, and oxide of manganese are got rid of. The solution is then acidulated with considerable excess of hydrochloric acid, and after complete reduction of the chromic acid, precipitated by ammonia. The oxide so obtained is not quite free from alkaline salts, but if it be redissolved and precipitated a second time (an operation which is indispensable) it will, after careful washing, be found practically free from all impurities.

J. W.

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**Separation of Iron Oxide from Uranium Oxide, and Estimation of Phosphoric Acid by means of Uranium.** By H. RHEINECK (*Chem. News*, xxiv, 233).

DISSOLVE the mixed oxides in nitric acid, nearly neutralise with sodium carbonate, add sodium acetate, and dilute with water to fifty times the weight of the oxides present; then heat the mixture on a water-bath, when the iron oxide will be precipitated. Some of the precipitate thus produced which had not been thoroughly washed, was found, after standing some time, to be mixed with a crystalline body, which could only be removed by heating with a large quantity of water.

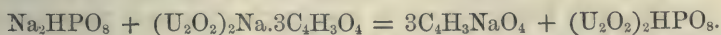
A similar substance is also produced when sodium acetate is added to any aqueous solution of uranium. The analysis of the compound, prepared in this manner, indicates the formula  $(U_2O_2)_2Na.3C_4H_3O_3$ ,\* which is the salt described by Wertheim as obtained by mixing acetic acid combinations of uranium and soda in aqueous solution.

For the volumetric estimation of phosphoric acid, the author prefers to take of the double salt 23.6 grm. to 1 litre of water, so that 1 c.c.

\* Equivalent formulæ are used in this paper.

indicates 0.00355 grm. of  $\text{PO}_5$ . The mode of procedure is similar to that recommended by Stohnmann.

It was found that the action of sodium phosphate on the double salt can be expressed by the equation—



A. T.

**Estimation of Glucose.** By F. JEAN (Compt. rend., lxxiii, 1397).

MILLON and Commaille have shown that cuprous oxide in solution precipitates an equivalent quantity of silver in the metallic state from an ammoniacal solution of silver chloride. This fact has been utilised by the author thus: the precipitate of cuprous oxide produced in an alkaline cuprotartrate solution, is dissolved in hydrochloric acid, supersaturated with ammonia, and mixed with excess of ammonia-nitrate of silver; and the resulting precipitate of metallic silver is weighed: the test-numbers given are satisfactory.

C. H. G.

**Estimation of Citric Acid.** By J. CREUSE (Pharm. J. Trans. [3], ii, 547).

THE process devised by the author for the estimation of citric acid, depends upon the precipitation of an alkaline citrate by barium acetate, the resulting barium citrate being perfectly insoluble in alcohol of 805 sp. gr., while the alkaline acetates and barium acetate are freely soluble in that liquid. The presence of alkaline acetates does not in any way interfere with the reaction. If the citric acid is already in combination with an alkali, one or two grams of the salt are dissolved in 20 c.c. of water, and the solution exactly neutralised with ammonia or acetic acid as may be required; a slight excess of barium acetate is then added, and afterwards twice its volume of alcohol of 95°. The whole is then allowed to remain undisturbed for 24 hours. The barium citrate which at first resembles a thick jelly, has by that time become denser and easier to wash. The precipitate is then thrown on a filter, washed with alcohol 63° and dried at a moderate heat.

To obtain accurate results, it is necessary to estimate the barium in the precipitated citrate. The filter is therefore burnt, and the ashes together with the precipitate ignited gently with a few drops of sulphuric acid, until a constant weight is obtained. Every three molecules of barium sulphate obtained represent one molecule of citric acid.

When it is required to estimate the citric acid of a non-alkaline citrate, soluble or otherwise, a certain weight of the salt is first heated carefully with a solution of caustic potash, the heat being applied sufficiently long to decompose the salt thoroughly, but not to such an extent as to alter the citric acid. The liquid is then filtered, and the filtrate, after neutralisation with acetic acid, treated as a solution of an alkaline citrate.

The author does not give any test-analyses, but appends several

analyses of metallic citrates; principally the double salts of bismuth with the alkalis, which are of variable composition.

A peculiar class of quadruple citrates is briefly alluded to, in which an alkaline citrate plays the part of a base, and a certain metallic salt the part of an acid. Thus phosphate, hypophosphite, valerate of iron, &c., were found to dissolve readily in solutions of the alkaline citrates, and to lose more or less entirely when thus combined, their special characteristics as salts of iron.

J. W.

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### Detection and Estimation of Earth-nut Oil in Olive Oil.

By A. RENARD (Compt. rend., lxxiii, 1330—1332).

THIS process is based upon the presence of arachidic acid in earth-nut oil. The oil to be examined is saponified, the soap decomposed by hydrochloric acid, and the resulting fatty acids converted into lead salts.

The oleate of lead is removed by ether, and the remaining salts are again decomposed by hydrochloric acid. The fatty acids are then dissolved in alcohol of 90°, and the solution left to cool. If earth-nut oil be present, abundant crystals of arachidic acid will soon be seen to form. The crystals are washed with alcohol of 70°, in which they are perfectly insoluble, dissolved in boiling absolute alcohol, and the solution is evaporated to dryness and weighed. In reckoning the amount of arachidic acid obtained, allowance must be made for the quantity dissolved by the alcohol of 90°. 100 parts of such alcohol at 15° dissolve .025 of arachidic acid.

The mean amount of arachidic acid found by the author in commercial earth-nut oil is 4.51 per cent. in oil expressed in the cold, and 4.98 per cent. in that expressed with the aid of heat.

This process will not succeed with a mixture containing less than 4 per cent. of earth-nut oil, but with a 10 per cent. mixture the result obtained by the author was within one per cent. of the truth.

J. B.

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### New Method of Estimating Morphine in Opium. By W. STEIN (Arch. Pharm. [2], cxlviii, 150—156).

THIS method is based on the reduction of iodic acid by morphine, the separated iodine being dissolved out by chloroform, and the quantity of morphine determined by diluting a quantity of the aqueous opium extract of given weight with known quantities of water, till on agitating the liquid with chloroform, the layer which rises to the surface no longer exhibits a perceptible brown colour.

The limit of dilution at which the coloration becomes imperceptible, must be determined by each observer for himself, by operating in a similar manner on a pure morphine solution of known strength: the author finds that his own eye is capable of detecting a tint equivalent to 1 pt. of morphine in 20,000 parts of water. Alcohol, acetic acid, hydrochloric acid, ammonia, and the fixed alkalis, prevent the appearance of the colour,



or retard it. Warming before addition of chloroform on the contrary promotes the reaction, but the solution must be allowed to cool again before the chloroform is added; if the liquid be not warmed, it will be necessary to wait at least half an hour before adding the chloroform.

Before proceeding to the actual estimation, it is necessary to remove certain bodies which act upon iodic acid in the same manner as morphine. This may be effected by treating the opium powder with cupric sulphate, extracting with water to which a few drops of sulphuric acid are added, then heating and filtering. The bodies prejudicial to the reaction remain on the filter, the morphine being contained in the filtrate.

The mode of performing the process is as follows: 0.1 grm. opium powder, and an equal or double weight of cupric sulphate or acetate are introduced into a small flask, moistened with a few drops of dilute sulphuric acid, then heated to boiling with 100 grams. of distilled water, and the whole is left to stand for a quarter to half an hour. The liquid is then filtered: 6 c.c. of the filtrate is mixed with about 6 centigrams of iodic acid and two or three drops of rectified sulphuric acid, and, as soon as the iodic acid is dissolved, 3 cub. cent. of chloroform free from alcohol is added. The mixture is then repeatedly shaken for a quarter of an hour, and left to stand to allow the chloroform layer to separate.

W. S.

### Estimation of Morphine in Opium. By JOHN T. MILLER (Pharm. J. Trans. [3], ii, 465—467).

THIS method is likewise based on the reduction of iodic acid by morphine. Aqueous iodic acid is added to a known weight of opium in solution, and after the lapse of a few minutes, the liberated iodine is washed out by shaking the mixture with carbon bisulphide. The *sample colour* thus produced is then compared with another, the *standard colour*, prepared in the same manner, but from a solution of morphine of known strength; and their intensity equalised by adding carbon disulphide to the deeper.

The results obtained by this process, although generally lower, are considered nearer approximations to the truth than those obtained by ordinary methods of precipitation.

The following table exhibits a few of the author's results:—

Percentage of crude morphine by Br. Pharm. process.	Weight of precipitate after washing with chloroform.	Amount of real morphine in precipitate by new process.	Percentage of real morphine by new process.
10.2	9.3	7.81	8.1
6.4	6.1	5.76	6.43
9.5	8.7	7.4	8.48
17.4	15.8	14.0	14.2

A. T.

*Method of Assaying Silver adopted in the Assay Offices of the Indian Mints.* By H. E. BUSTEED (Chem. News, xxiv, 243, 259).

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*Assay of Gold and Silver.* By T. W. BLOSSOM (Chem. News, xxiv, 14, 42, 269).

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*New Form of Gas-Apparatus.* By JOHN PARRY (Chem. News, xxiv, 282).

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### Technical Chemistry.

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**Manufacture of Red Lead.** By G. MERCIER (Ann. Ch. Pharm., clx, 252—256, in abstract from Ann. des Mines [6], xix, 1).

THE usual process of manufacture of red lead by exposing massicot in trays in the same furnace that serves for the production of the massicot, is tedious, and very often gives an extremely small yield. This is evidently due to the changes of temperature to which in such a furnace it is of necessity exposed.

The principal thing to be attended to, next to access of sufficient air, is constancy of the right temperature; for the temperature at which massicot takes up oxygen, and that at which red lead loses it, lie very near each other. The most favourable temperature for the formation of red lead approaches that of a dull red heat, without however, reaching it.

The greatest beauty in the red lead corresponds to the greatest increase in weight in the massicot: this is about 2 per cent. But after the maximum weight is reached, the brilliancy of the red lead can still increase or diminish through a change in its molecular condition.

The author has constructed a furnace for use on the large scale, best adapted for the manufacture of red lead. It is essentially a large muffle, round which the fire plays in a great number of small channels. By means of easily worked dampers in certain of these channels, the heat can be regulated at pleasure in that part of the furnace. By this furnace in full action, and continuously worked, about 4 tons of red lead may be produced in 24 hours.

E. D.

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**Changes in the Quality of Well-Waters arising from their Proximity to Cemeteries.** By JULES LEFORT (J. Pharm. Chim., t. 4, xix, 330—337).

THE author has sought to determine if the water of wells situated at considerable distances from cemeteries can be contaminated with the products of the decay of nitrogenous organic matter. From obser-

vations made in Saint-Didier (Allier) he concludes that the evidence of contamination may be found in wells situated beyond the limits legally prescribed. By a decree of the 7th March, 1808, it is forbidden to sink a well within 100 meters of the graveyard.

T. E. T.

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### Experimental Inquiries into the Properties of Drying Oils.

By M. SACC (Compt. rend., lxxiii, 1274—1276).

2,500 GRAMS of raw linseed oil boiled for ten minutes with 30 grams litharge and 30 grams of minium, then cooled in a close vessel and weighed at the end of 24 hours, lose only 60 grams in weight. This loss is so small that boiled linseed oil may be regarded as a simple isomeric modification of the raw oil.

Linseed oil boiled until it loses 5 per cent. of its weight, assumes the consistence of molasses, and changes into a mass resembling caoutchouc when it has lost 12 per cent.

To test the drying properties of these preparations they were applied to the same deal board. That boiled for ten minutes was transformed at the end of 24 hours into a fine transparent varnish; that which was of the consistence of molasses was not resinified at the end of 15 days; and that which had passed into the state of caoutchouc remained unaltered. The increased drying properties of boiled linseed oil are therefore not due to concentration of the oil.

To prove that the resinification of linseed oil is due to absorption of oxygen, thin layers of the oil were laid upon plates of zinc, and it was found that an increase in weight took place during resinification equal to about half the weight of oil used. The thinner the layers of oil, the more quickly they dry, and at 5° the absorption of oxygen is one-half less rapid than at 15°.

J. B.

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### Composition and Heat of Combustion of Lignites. By

A. SCHEURER-KESTNER and C. MEUNIER (Compt. rend., lxxiii, 1332—1336).

I. HARD lignite from Fadeau (Bouches-du-Rhône): black compact mass, with dull conchoidal fracture.

II. Rich lignite from Manosque (Basses-Alpes): friable mass, having an unctuous aspect, black colour, and uneven fracture.

III. Hard lignite from Manosque: black compact mass, with shining conchoidal fracture.

IV. Rich lignite from Bohemia: compact mass, with uneven fracture, black and shining.

V. Lignite passing into fossil wood, from Bohemia: aspect dull in the direction of the woody fibres, shining in the transverse direction. The fracture displays a stratification of closely lying layers.

VI. Fossil wood passing into lignite: much resembles the preceding.



	I.			II.			III.		
	Crude.	Pure.	Volatile part.	Crude.	Pure.	Volatile part.	Crude.	Pure.	Volatile part.
Water....	8·27	—	—	1·00	—	—	7·82	—	—
Carbon ..	55·30	72·98	25·78	55·26	70·57	13·91	56·68	66·31	36·75
Hydrogen..	3·06	4·04	11·09	4·26	5·44	10·37	4·15	4·85	9·10
Oxygen ..	17·41	22·98	63·13	18·78	23·99	45·72	24·65	28·84	54·15
Ash .....	15·96	—	—	20·70	—	—	6·70	—	—
	100	100	100	100	100	100	100	100	100
	Heat-units.			Heat-units.			Heat-units.		
Heat of combustion observed	6483			7363			6991		
„ calculated by Du- long's law .....	6295			6533			5782		
Sum of heats of combus- tion of elements .....	7270			7551			7006		

	IV.			V.			VI.		
	Crude.	Pure.	Volatile part.	Crude.	Pure.	Volatile part.	Crude.	Pure.	Volatile part.
Water....	2·39	—	—	10·41	—	—	10·60	—	—
Carbon ..	72·03	76·58	68·95	57·06	66·51	32·56	57·72	67·60	33·28
Hydrogen..	7·78	8·27	10·97	4·05	4·72	9·50	3·89	4·55	9·38
Oxygen ..	14·24	15·15	20·08	24·68	28·77	57·94	23·78	27·85	57·34
Ash .....	3·56	—	—	3·80	—	—	4·01	—	—
	100	100	100	100	100	100	100	100	100
	Heat-units.			Heat-units.			Heat-units.		
Heat of combustion observed	7924			6358			6311		
„ calculated by Du- long's law .....	8343			5759			5827		
Sum of heats of combus- tion of elements .....	8999			6979			7010		

Except in one case, in which the amount of hydrogen is very high, the heat of combustion is greater than that calculated according to the law of Dulong; and in all cases it is less than the sum of the heats of combustion of the elements, carbon and hydrogen. In this respect the lignites are distinguished from coal, which always gives a calorific power greater than that of the carbon and hydrogen. It is impossible, therefore, to judge of the value of a combustible of this kind from its elementary composition.

J. B.

**Temperatures of Inflammation and Detonation of Explosive Compounds.** L. LEYGUE and P. CHAMPION (Compt. rend., lxxiii, 1478).

Priming powder for Chassepot .....	191
Fulminate of mercury .....	200
Powder formed of chlorate of potash 1 part, sulphur 1 part .....	200
Abel's protoxide (paper-pulp) .....	205
Gun-cotton .....	220
Powder formed of sulphide of antimony 1 part, chlorate of potash 1 part .....	280
Shooting powder .....	288
Gunpowder .....	295
Picrate of mercury } Picrate of lead } Picrate of iron }	detonate..... 296
Picrate powder for torpedoes .....	
Picrate musket powder .....	
Picrate gunpowder .....	380
Artificial saffron .....	315
Picric acid, picrate of magnesia, of ammonia, of potash .....	336
Nitroglycerin detonates .....	256—257
Inflammation of sulphur in the air .....	246

J. B.

**Recovery of Sugar from Molasses by Baryta.** By G. LUNGE (Dingl. polyt. J., ccii, 164—169).

THE solution of baryta is evaporated in an ordinary vacuum-pan to such a point that it would set solid if allowed to cool, then run straight into a number of iron boxes, which, when filled, can be lifted by two men. A certain quantity of molasses is immediately run into the hot baryta. The mass sets in a few minutes, and is then emptied into an iron cistern capable of holding the contents of 100 of the boxes, and having a pierced false bottom covered with a linen cloth. The mass is allowed to drain in this cistern for a considerable time, and is then washed with water as long as any colour is extracted.

The washed sugar-baryta, still containing excess of baryta and sulphide of barium, is then mixed with water in other cisterns, and treated with a current of carbonic acid proceeding from the fermentation of the uncrystallisable sugar first drained from the mass of sugar-baryta. The syrup of sugar is separated from the deposited carbonate of baryta, partly by subsidence and partly by the use of filter-presses, and the still remaining sulphide of barium is got rid of by successively adding a solution of sulphate of zinc in very slight excess, and then sulphate of alumina, which forms (it is said) an insoluble double salt with that excess. This solution of sugar, treated as any other, yields a product pure enough to go into direct consumption.

The remainder of the paper is devoted to the preparation of potash-salts from the residues of fermentation.

C. H. G.

**Application of Oxygen to the Freeing of Petroleum Springs from Paraffin** (Dingl. polyt. J., ccii, 194, from the "San Francisco Scientific Press," 1871, 98).

OXYGEN, under high pressure, is conveyed, by means of piping, to gradually increasing depths in the borings, &c.; the flame starting at the mouth, naturally descending with it, burns or melts the deposit of solid paraffin which impedes the flow of the oil.

Nothing is said as to the material of which the pipes are made.

C. H. G.

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**Blumer's New Aniline Blue for Printing** (Dingl. polyt. J., ccii, 193).

BLUMER-ZWEIFEL has patented a process by which he produces a new analine-blue. He prepares a paste from 100 grams starch and 1 litre water, and adds to it while warm 40 grams chlorate of potash, 3—4 grams iron vitriol (Eisen-vitriol), and 10 grams sal ammoniac. The well mixed paste is then fully cooled and mixed with 60 grams hydrochloride of aniline, and immediately used. Instead of the hydrochloride the tartrate of aniline may be used. The printed goods are oxidised, then passed through warm or faintly alkaline water whereby the blue colour is developed.

C. H. G.

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**The Impregnation of Wood for Use in Mines, &c.** (Dingl. polyt. J., ccii, 174—182).

AN exposition of the various processes employed from time to time for this purpose, and an account (incomplete) of certain comparative experiments on the value of some of them. As a general result it may be stated that the impregnation of wood with sulphate of copper, or with creosote oils, or their vapours, is of service in rendering the wood three or four times as lasting as unprepared material of the same quality. It has also been found that wood well soaked in the brine from salt-works, lasted in good condition for 13 years in a brown coal mine where untreated wood had to be changed every two years.

C. H. G.

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**Use of Molybdic Acid in Dyeing** (Dingl. polyt. J., ccii, 192).

REMARKS that as yet no useful results have been obtained with this material, but that the subject merits further attention.

C. H. G.

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**Pyrometric Researches on a Clay from Eisenberg.** By C. BISCHOF (Chem. Centr., 1871, 719).

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**Fabrication of Caustic Baryta and Sulphide of Barium.**

By Dr. G. LUNGE (Dingl. polyt. J., ccii, 76—80).

A DESCRIPTION of the work actually done in a French factory, where large quantities of these bodies are prepared for use in recovering sugar from molasses.

C. H. G.

**Coating of Metallic Articles with a nearly costless, Permanent, Shining Black Coat.** By C. PUSCHER (Dingl. polyt. J., ccii, 92).

THE bodies to be coated are supported above the surface of some coal-dust strewn over the bottom of an iron box fitted with a lid, and the box is then set on a brisk fire. The vapours given off from the coal cover all the articles with an even black coat, which is not sticky, and has no smell even when hot.

C. H. G.

**The Colouring of Veneers.** By C. PUSCHER (Dingl. polyt. J., ccii, 95).

THE raw veneer, soaked for half an hour in a 10 per cent. caustic soda solution, and then well washed, takes colour through and through. As it becomes soft and leathery, it is necessary to dry it, after staining, under pressure between pasteboards.

C. H. G.

**Porcelain Photography in America.** (Chem. Centr., 1871, 684.)

SIMPLY prints taken from an ordinary negative on an albuminised and collodionised surface of porcelain, instead of on paper. They are not burnt in.

C. H. G.

**Tartaric Acid Making.** By M. KURTZ (Chem. Centr., 1871, 713—716).

THE subject is naturally divided into two parts. The preparation of tartrate of lime, and that of tartaric acid from the latter. Each branch is fully treated, but there does not appear to be anything new, except in the details of working.

C. H. G.

**Application of Glycerin to Mercerise and Mordant Vegetable Fibre.** By A. BURGEMEISTER (Chem. Centr., 1871, 720).

IF ordinary sulphate of iron be first mixed with glycerin and then with an excess of caustic alkali, a nearly colourless solution is obtained, which does not deposit any ferrous oxide, even at the boiling heat, but gives up its iron almost to the last trace to vegetable fibre, which

thereby becomes mordanted in a more thorough manner than is possible when acid solutions are employed. The excess of alkali present prepares the cloth to take the iron, and removes the "dead" fibres at the same time. The process is in use in England.

C. H. G.

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**Printing-colours for Artificial Alizarin.** By Dr. H. GROTHE (Dingl. polyt. J., ccii, 83—86).

A NUMBER of recipes based on the use of a paste containing 10 per cent. of real colouring matter.

C. H. G.

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**Casein as Thickening for Colour-printing.** (Dingl. polyt. J., ccii, 94). From Bulletin de la Société industrielle de Mulhouse.

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**Potato-testing with Solution of "Salt."** By Dr. W. SCHULTZE (Dingl. polyt. J., ccii, 86).

SHOWS that the method, based on the use of solutions of salt of known densities, is troublesome and inaccurate.

C. H. G.

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**Oxide of Iron for Purification of Coal-gas.** (Dingl. polyt. J., ccii, 91).

DRAWS attention to the fact that natural ferric oxide is applicable to the purification of gas, and that another source of an analogous material is found in the residues of the aniline factories.

C. H. G.

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**Dyeing Alpaca with Iodine-green** (Dingl. polyt. J., ccii, 193).

SOME criticisms of a former paper with the same title.

C. H. G.

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**Estimation of the Melting and Setting Points of Commercial Paraffins** (Dingl. polyt. J., ccii, 193).

NOTHING new. A chip of paraffin is thrown on the surface of hot water, the temperature of which is observed at the moment when the melted drop loses its transparency.

C. H. G.

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**Alum Crystallisation.** By ALBERT STIASSNY (Dingl. polyt. J., ccii, 191).

ALUM was obtained crystallised in rhombic dodecahedrons from a solution of alum to which a little potash had been added. A similar result was obtained with iron and chrome alums, but the crystals were not so regular.

C. H. G.

## PAPERS READ BEFORE THE CHEMICAL SOCIETY.

VII.—*On the Composition of Natural Tantalates and Niobates.*

By C. RAMMELSBERG, Member of the Academy of Sciences of Berlin.

THE minerals containing *tantalum* and *niobium* occur only in a few localities of the globe, and there only in small quantities. They are principally found in the granitic rocks of Scandinavia, Finland, the Ural (the Ilmen mountains, near Miask), Bavaria (Bodenmais), France (Limoges), the United States (Massachusetts, Connecticut, New Hampshire), and Greenland. Besides those minerals the principal elements of which are formed by tantalum and niobium, many others may exist containing only traces of these rare elements, but it is still very difficult in such cases to detect them; we know, however, that tin-stone (Zinnstein) and wolfram belong to this class.

The history of the mineralogical and chemical investigation of the tantalum minerals, begins in 1801, when Hatchett, in a black mineral from Massachusetts, afterwards named columbite, found a new metallic oxide, "columbium oxide;" and precisely at the same time, Ekeberg, in a similar mineral from Kimit, in Finland, called tantalite, and in another from Ytterby, in Sweden, named yttrotantalite, detected a new oxide, called "tantalum oxide." Some time afterwards Wollaston asserted that columbium oxide and tantalum oxide were identical, and in consequence the name "tantalie acid" was then adopted by chemists.

The chemical properties of the combinations of tantalum were investigated by Berzelius, who used in his experiments only the Finnish and Swedish tantalites, or the acid extracted therefrom. To him we are also indebted for the method of analysing these minerals with bisulphate of potash.

The number of the tantalum minerals was increased by pyrochlore fergusonite, aeschynite, euxenite, polycrase, samarskite and others, and analyses were published by Wöhler, Hartwall, Hermann, Scheerer, N. and A. Nordenskiöld; but the most successful researches in this department of science are the work of Henry Rose.

In the year 1835, Breithaupt asserted that tantalite (columbite) is isomorphous with wolframite; likewise fergusonite with scheelite. Gustav Rose, in 1845, pointed out by special researches, that columbite has really the form and angles of wolframite; and Henry Rose was thereby induced to investigate more especially the minerals and



combinations of tantalum, and to inquire into the cause of the great differences of specific gravity observed by Wollaston, in the tantalic acid of Finnish tantalites on the one hand, and of Bavarian or American columbites on the other.

This was the beginning (in 1840) of the memorable series of researches continued by Henry Rose for twenty years till his death. The discovery of a new element, niobium, was a splendid result of this great, laborious, and, in every sense, difficult investigation, and history will for ever attribute to it an honourable place in science. And although the celebrated founder of Analytical Chemistry failed to discover the right path, nevertheless young chemists, in studying that long series of memoirs on tantalum and niobium, published in *Poggendorff's Annalen*, will be able to trace it out for themselves, and will also understand by what circumstances the guide was diverted from the right way and fell unconsciously into error.

In 1844 H. Rose declared his belief that the metallic acids of the Swedish and Finnish tantalites were one and the same, viz., the true tantalic acid described by Berzelius, but that the tantalites or columbites from Bodenmais and America contained two acids, one much resembling tantalic acid, or perhaps identical with it; the other a new acid, which he named *niobic acid*. These results were deduced from the study of the volatile chlorides formed by heating the acids of those minerals mixed with charcoal in chlorine. By this treatment the acid of the Bodenmais tantalite yielded two different chlorides, one of which was yellow, fusible, and comparatively more volatile; the other, white and infusible. On decomposing the latter with water, and treating the acid thereby separated with carbon and chlorine, both chlorides again appeared; but after several repetitions of the process the acid gave only the white chloride, niobium chloride, which was changed by water into niobic acid.

In 1846 H. Rose, after a long series of researches, became convinced that the second acid of the columbites was not identical with tantalic acid, though very similar to it. He named it *pelopie acid*, and stated that the yellow tantalum chloride was so like pelopie chloride, that a long series of experiments had been necessary to convince him that the two were not identical, pelopie acid having indeed very much the appearance of tantalic acid mixed with niobic acid. Seven years afterwards he became still further convinced of the separate identity of niobic and pelopie acid, but at the same time a very remarkable connexion between the two acids came to light.

When pure niobic acid was mixed with a very large quantity of carbon and slightly heated in chlorine, only the yellow chloride appeared, but the acid separated therefrom gave, when treated in the same manner, both chlorides, the yellow and the white. Hence it fol-

lowed that both were combinations of the same element, and as the yellow (pelopic chloride) contained a larger proportion of chlorine, pelopic acid must be a higher degree of oxidation than niobic acid. A long time elapsed, however, before Rose determined on changing the adopted designation, but in 1852 he resolved to change the name of pelopic acid into niobic acid, and that of the former niobic acid into hyponiobic acid.

The formula of tantalic acid had been taken by Berzelius as  $Ta_2O_3$ ; Rose adopted  $TaO_2$ , and likewise for niobic acid  $NbO_2$ ; for hyponiobic acid  $Nb_2O_3$ .

It is easy to conceive that two chlorides can be formed in the same process; various examples of such formation may indeed be adduced; but Rose never succeeded in changing niobic acid by reducing agents into hyponiobic acid or in oxidising the latter. The change of the one acid into the other could be effected only through the medium of the chlorides; and moreover not directly, for Rose has not shown that the yellow hyponiobic chloride is changed by chlorine into the white niobic chloride.

With regard to the natural combinations, it was thus far established that Swedish and Finnish tantalites and yttrotalite contain tantalic acid,  $TaO_2$ , whereas the columbites from Bavaria, North America, Greenland, and the Ural contain hyponiobic acid,  $Nb_2O_3$ .

Marignac, by a series of very important researches, had found that the fluorides of silicium, zirconium, titanium, and tin, combined with those of mono- or bi-valent elements, are isomorphous, so that the corresponding acids must be regarded as  $RO_2$ , an essential argument for the formula  $SiO_2$  of silicic acid.

It is generally known from former experiments of Berzelius that molybdates and tungstates cannot be changed into fluorides, even by an excess of hydrofluoric acid, only half the oxygen being replaced by fluorine. The combinations thereby generated, viz., fluoxymolybdates and fluoxytungstates, are, according to Marignac, isomorphous with the double-fluorides of the quadrivalent elements above mentioned.

Marignac treated the metallic acid of the Bodenmais columbite, *i.e.*, the hyponiobic acid of H. Rose, with hydrofluoric acid and fluoride of potassium, and found that a fluoxyniobate is formed, which may be converted into a pure fluoride of niobium and potassium by an excess of hydrofluoric acid, but is again decomposed by water. The analytical examination of these salts showed that niobic fluoride must contain 5 atoms of fluorine.

On that occasion Marignac observed an important fact. When the metallic acid of the columbites was dissolved by hydrofluoric acid and fluoride of potassium, the solution gave at first a certain quantity of a sparingly soluble salt, easily recognised as the well known fluoride of



tantalum and potassium; after its separation the oxyfluoride of niobium and potassium was deposited in crystals, easily soluble in water. Another remarkable fact was the isomorphism of the double fluorides of tantalum and of niobium; and on the other hand, that of the fluoxy-tungstate, -molybdate and -niobate of potassium.

The white hyponiobic chloride of H. Rose was recognised by Marignac and by H. Deville as an *oxychloride*; the yellow niobic chloride was found to be free from oxygen; the analyses and the vapour-density gave the formulæ,  $\text{NbOCl}_3$  and  $\text{NbCl}_5$ .

These new and unexpected results were also confirmed by Blomstrand, who affirmed that all tantalites and columbites contain two acids, and that niobic acid gives a yellow chloride and a white oxychloride. He adopted also as the formulæ of the acids,  $\text{Ta}_2\text{O}_5$  and  $\text{Nb}_2\text{O}_5$ .

It may now be seen by what circumstances H. Rose was led into error. At first he had seen quite rightly, that columbites contain two different metallic acids, niobic acid and another (pelopic acid), closely resembling tantalic acid. But he fell into error when he obtained only a yellow chloride from his niobic acid, and believed it to be identical with that produced from the crude acid of the mineral. We now know that the first, formed from the white oxychloride, was pure niobic chloride, whereas the latter was a mixture of the chlorides of tantalum and niobium. Such an error was very excusable, for the two chlorides agree closely in every character, differing only by a few degrees in their melting and boiling points. It is only by studying the fluorides that it is possible to detect the presence of tantalum and niobium. Indeed, it is a strange accident that H. Rose, the discoverer of the volatile oxychlorides of chromium, molybdenum, and tungsten, regarded a similar compound of niobium as a pure chloride—just the same error as Berzelius fell into in taking vanadium oxychloride for chloride—a mistake which remained undetected till Roscoe, in an excellent research, explained this point, and gave to vanadic acid the formula  $\text{V}_2\text{O}_5$ , corresponding to those of tantalic and niobic acid, thereby explaining the isomorphism of vanadate, phosphate, and arseniate of lead, which I discovered some years ago.

The new facts concerning tantalum and niobium throw great light on the researches of H. Rose, for it is easy to understand that his hyponiobic acid was pure niobic acid, and therefore that all facts, depending thereon, are of full value for science. Such a critical review I have given in *Poggendorff's Annalen*, cxxxvi, 177.

The historical view here given will prove that the true composition and constitution of all minerals containing tantalum and niobium is still unknown, in spite of numerous analyses we possess thereon. It will be necessary to investigate the nature of their metallic acids, to determine whether it is pure tantalic or niobic acid, or a mixture of the two, and then



to separate them by analytical means. Marignac and Blomstrand have published only a few notices relating to the quantities of the two metallic acids in columbites, whereas I myself have undertaken a complete examination of all minerals belonging to that class, as far as their rarity permits.

But besides this point, many other difficulties are met with in such an attempt. Many of the tantalum and niobium minerals contain titanium, zirconium, thorium, and the group of elements designated as yttrium, often associated with cerium and its congeners. All analytical methods hitherto known for separating these rare substances, are incomplete; it was therefore necessary to find new ways, and that was possible only by a special study of the properties and the behaviour of those elements.

In the present paper I shall describe the results of the examination of all the tantaliferous minerals I could procure, viz., tantalite (columbite), yttrotantalite, fergusonite, pyrochlore, euxenite, polycrase, and some others, omitting the details of the analytical processes, and giving only some account of the principal operations.

*I. Determination and Separation of the Metallic Acids.*—Some of the minerals contain principally tantalum and niobium, associated with small quantities of tin, tungsten, and titanium, *e.g.*, tantalite, tapiolite, yttrotantalite, fergusonite, hjelmite. Another series consists of those which contain niobium (tantalum) and titanium, sometimes associated with traces of tin, tungsten, &c., *e.g.*, pyrochlore, euxenite, polycrase, &c. To a third class belongs woehlerite, which contains niobium, zirconium, and silicium.

The decomposition of these minerals is mostly effected by fusing them with bisulphate of potash. The mass is treated with water, whereby tantalic and niobic acid are left, and the electro-positive elements are dissolved. H. Rose has described very minutely the mode of proceeding, and how to separate tin and tungsten mixed with the insoluble acids, by fusing them with sulphur and carbonate of soda. The purified acids of tantalum and niobium are heated with acid fluoride of potassium ( $\text{HKFl}_2$ ), the mass is digested with water and a sufficient quantity of hydrofluoric acid, and the solution is brought to crystallisation. If tantalum be present, a greater or smaller quantity of acicular crystals is soon deposited, consisting of fluoride of tantalum and potassium =  $\text{K}_2\text{TaFl}_7$ .

This salt requires 130—200 parts of water for solution; it may, therefore be easily recognised even in small quantity. It is separated, and the mother-liquor evaporated a little, to separate the rest of the salt. By fractional crystallisation it is not difficult to obtain the whole quantity of tantalum in the form of this double fluoride. It might be dried and weighed, but I found it more accurate to decompose it

with sulphuric acid, and to determine the tantalic acid directly. The mother-liquor must be highly concentrated before the small prisms of the fluoxyniobate,  $K_2NbOFl_6$ , appear. If a direct determination of niobic acid is required, the whole is evaporated with sulphuric acid, and the residue treated with water.

Much more difficult is the separation of niobium (tantalum) and titanium. After fusing with bisulphate of potash and treating with cold water for some time, a great part of the titanic acid is dissolved, but in the way proposed by H. Rose no sufficient separation can be effected. It is, therefore, better to treat the fused mass with water kept in constant ebullition, whereby titanic acid is precipitated almost completely. The acids are heated with  $HKFl_2$ , and the fluorides,  $K_2TiFl_6$  and  $K_2NbOFl_6$ , are dissolved in water. Being isomorphous, they cannot be separated by crystallisation, notwithstanding that the former requires 60 to 70 parts of water for solution. Marignac proposed to treat the liquid mixed with hydrochloric acid with zinc, excluding the air, till the colour indicates the reduction of titanic acid to titanic sesquioxide, and to determine the oxygen lost by means of a standard solution of permanganate of potash. I have operated in this manner, but I prefer another method, namely, boiling the liquid with a weighed quantity of copper, and weighing the residue after the solution has acquired a green colour. By direct experiments with weighed quantities of  $K_2TiFl_6$ , I had previously determined the quantity of copper necessary for reduction. Both methods are indirect and of no great accuracy, but sufficient for an approximate determination.

II. *Determination of Yttrium, Erbium, Cerium, Lanthanum, and Didymium.*—These elements occur in many minerals of the class, and are occasionally associated with calcium, uranium, and iron. After being fused with bisulphate of potash and treated with water, all these substances are dissolved as sulphates. Oxalic acid precipitates all, except uranium and iron. The oxalates are strongly heated, the oxides redissolved in hydrochloric acid and precipitated by ammonia to separate them from lime, and the precipitate is dissolved in dilute sulphuric acid. We have now to separate the metals of the yttrium and the cerium group.

Mosander had first declared yttrium to be a mixture of three different elements, yttrium, erbium, terbium. The further experiments of Marc Delafontaine seemed to confirm that opinion, but in a very interesting series of researches by Bunsen and Bahr, only two different metals, yttrium and erbium could be obtained from the crude yttria of gadolinite. My own experiments agree with these results.

There is but one known method of separating the yttrium and cerium metals, for which we are indebted to Berzelius. A solution



of their sulphates, mixed and saturated with sulphate of potash, gives, after standing for some time, a crystalline precipitate of double sulphates, which contains the cerium metals and sometimes a part of the yttrium metals. By washing it with a saturated solution of sulphate of potash, the double sulphates of the yttrium metals are dissolved. I cannot here enter into a more special discussion of the precautions necessary for a satisfactory separation. The yttrium metals are precipitated by oxalic acid, heated to strong redness, and weighed. From the quantity of sulphates given by a known weight of them, the proportion of yttria ( $YO$ ), and erbia ( $ErO$ ) is easily calculated by the aid of a simple formula given by Bunsen. I need not describe the methods of determining cerium, lanthanum, and didymium, and of separating uranium and iron. Besides these operations, which occur most frequently in analyses of such minerals, there are a few others which are necessary in particular cases, *i.e.*, when *zirconium* or *thorium* occurs in tantalates and niobates. It is well known that these elements exhibit in their reactions the closest resemblance to titanium as well as to the cerium and yttrium metals, so that their detection and separation offer the greatest difficulties. After melting the substance with bisulphate of potash, zirconium sulphate and thorium sulphate are partly dissolved in the acid liquid, and the latter is completely precipitated by oxalic acid, together with the cerium and yttrium metals. The oxalates are changed into oxides by heating to strong redness, and when these oxides are treated with hydrochloric acid, thoracic acid ( $ThO_2$ ) remains wholly insoluble. It must then be melted with bisulphate, dissolved in water, and heated with hyposulphite of soda, by which means it is precipitated and can be separated from the oxides of cerium, the usual associates of thorium.

Zirconium is often said to occur in our mineral group, but I believe, that in many cases there has been an error. Zirconic acid ( $ZrO_2$ ) must be searched for in analysis, both in the insoluble part of the metallic acids and in the acid solution. The former are changed into double fluorides of potassium. As those of zirconium are difficultly soluble and form very distinct crystals, the presence of zirconium is easily detected. When the acid solution, containing cerium, yttrium, uranium, iron, &c., is precipitated by an excess of oxalic acid, zirconium oxalate re-dissolves, and may be precipitated by ammonia together with uranium and iron. After heating and reducing by a current of hydrogen, hydrochloric acid dissolves the iron, aqua regia the protoxide of uranium, leaving the zirconia, if there is any present.

I shall now give the results of my own analyses of the tantalum minerals, which enable us to calculate their composition and express their constitution by formulæ. It will, then, be understood what connection exists between their crystalline form and their chemical consti-



tution. In calculating the numbers obtained by experiment, I have adopted the following atomic weights:—

$$\text{Ta}^v = 182; \text{Nb}^v = 94.$$

$$\text{Th}^{iv} = 234; \text{Zr}^{iv} = 90; \text{Ti}^{iv} = 48.$$

$$\text{Er}'' = 112.6; \text{Y}'' = 61.7.$$

$$\text{Di}'' = 96; \text{Ce}'' = \text{La}'' = 92.$$

$$\text{U}'' = 120.$$

Sn, W, Fe, Mn, Ca, Na, &c., are known.

### I. *Tantalite and Niobite (Columbite).*

All minerals designated by these names form an isomorphous group of the same composition, their principal constituents being formed by the molecules—

Tantalate of iron. . . . .  $\text{FeTa}_2\text{O}_6$ , and

Niobate of iron . . . . .  $\text{FeNb}_2\text{O}_6$ .

They differ only in the relative proportions of the two, tantalites being richer in the tantalate, niobites containing a predominant quantity of the niobate, so that the best crystallised variety, the niobite of Greenland, contains only some few per cent. of tantalum, and seems to be nearly pure niobate.

#### A. *Tantalite.*

While Berzelius and H. Rose found in Finnish and Swedish tantalites only one metallic acid, Hermann, in 1857, asserted that the Kimito tantalite contained two, namely, besides tantalic acid, which he designed as “tantalous acid” (tantalige Säure), another, to which he gave the name “ilmenige Ilmensäure”; this latter, however, by its properties, specific gravity (5.5), and its reactions with hydrochloric acid and zinc (brown colour), is evidently nothing but niobic acid.

To my own analyses I shall here add the few for which we are indebted to Hermann and Marignac.

I. From Härkäsaari (Tammela) in Finland: sp. gr. = 7.384; powder brownish black.

II. From Rosendal (Kimito) in Finland: sp. gr. = 7.277; powder brownish black.

III. From Kimito; analysed by Hermann.

IV. From Skogböle (Kimito): sp. gr. = 7.272; powder blackish.

V. From Skogböle (ixiolite of A. Nordenskiöld): sp. gr. = 7.232; powder brownish black.

VI. From Sweden, perhaps from Broddbo: sp. gr. = .03; determination of the metallic acids by Marignac.

VII. From Broddbo, near Fahlun: sp. gr. = 6.311.

VIII. From the same locality, but somewhat doubtful, sp. gr. 6.082.

	I.	II.	III.	
			<i>a.</i>	<i>b.</i>
Tantalie acid.....	76·34	70·53	73·07	68·30
Niobic acid.....	7·54	13·14	11·02	9·33
Stannic acid.....	0·70	0·82	0·70	6·94
Titanic acid.....	—	—	—	0·61
Tungstic acid.....	—	—	—	—
Protoxide of iron.....	13·90	14·30	12·40	9·49
Protoxide of manganese.....	1·42	1·20	1·32	5·33
	99·90	99·99	98·51	100·

	IV.	V.	VI.	VII.	VIII.
Tantalie acid .....	69·97	63·58	65·60	49·64	42·15
Niobic acid.....	12·26	19·24	10·88	29·27	40·21
Stannic acid .....	2·94	1·70	6·10	2·49	0·18
Titanic acid.....	trace	—	—		—
Tungstic acid.....	—	—	—		—
Protoxide of iron.....	14·83	9·19	17·42	13·77	16·00
Protoxide of manganese }		5·97		2·88	1·07
	100·	99·58	100·	98·05	99·61

Calculating these analyses, we find that all tantalites may be included in the formula  $m\text{FeTa}_2\text{O}_6 + n\text{FeNb}_2\text{O}_6$ ,

and in I,  $m : n = 6 : 1$   
 II, „  $= 3 : 1$   
 III *a*, „  $= 4 : 1$   
 IV, „  $= 3 : 1$   
 V, „  $= 2 : 1$   
 VI, „  $= 4 : 1$   
 VII, „  $= 1 : 1$   
 VIII, „  $= 2 : 2$

Tantalites sometimes contain a considerable quantity of *tin*. Weber found in a Kimito tantalite more than 9 per cent. stannic acid; Berzelius in Broddbo tantalite 8 per cent.; in a Finbo tantalite, near 17 per cent., and it must be supposed that  $\text{FeSnO}_3$  is a constituent of tantalites, because in stanniferous varieties the atomic ratio of Fe and Ta(Nb) is no longer 1 : 2.

The isomorphism of wolfram and tantalite proves also that  $\text{FeWO}_3$  is an isomorphous constituent of tantalites (and likewise  $\text{FeTa}_2\text{O}_6$  occurs in wolfram).

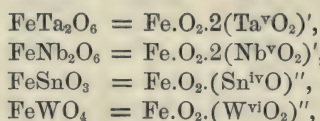
As *niobite* (columbite) we may designate those varieties which are richer in  $\text{FeNb}_2\text{O}_6$ . For these minerals, occurring at Bodenmais, in

the United States, and in Greenland, the numbers  $m$  and  $n$  are, according to the analyses of Blomstrand and Marignac:—

$m : n = 1 : 2.$	Bodenmais.
„ 1 : 3.	Bodenmais, Haddam.
„ 1 : 4.	Bodenmais.
„ 1 : 8.	Bodenmais, Akworth;

while the beautiful crystals from Greenland are nearly pure  $\text{FeNb}_2\text{O}_6$ .

The crystalline form of tantalites and niobites is the same, but tantalites rarely occur in determinable crystals. They belong to the rhombic system, and are isomorphous with wolframite. The isomorphism of the iron salts of  $\text{Ta}(\text{Nb})$ ,  $\text{Sn}(\text{Ti})$ , and  $\text{W}$ , *i.e.*, elements of different atomicity, is connected with analogous constitution, if we suppose—



comparing these salts to nitrates ( $\text{RN}_2\text{O}_6$ ), carbonates ( $\text{RCO}_3$ ), and sulphates ( $\text{RSO}_4$ ), derived from the mono- and bi-valent radicals  $\text{NO}_2$ ,  $\text{CO}$ , and  $\text{SO}_2$ .

The specific gravity of tantalites increases with the quantity of tantalate. The specific gravity of the tantalite of Tammela is 7.38; that of the niobite of Greenland is 5.38; that of tantalic acid is 7.6; that of niobic acid 4.5.

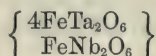
## II. *Tapiölite*.

A. Nordenskiöld found tetragonal crystals of a mineral from Sukkula, in Finland, which contains, according to my own analysis:—

Tantallic acid .....	73.91
Niobic acid.....	11.22
Stannic acid .....	0.48
Protoxide of iron .....	14.47
Protoxide of manganese..	0.81
	<hr/>
	100.89

Sp. gr. = 7.496.

It has the composition of a tantalite—



and proves that these compounds are heteromorphous.



III. *Fergusonite* (Yttrotantalite, Tyrite, Bragite).

The numerous older analyses of these minerals could not give a true idea of their composition, because neither the metallic acids nor the oxides of yttrium and erbium had been separated. My own results are as follows:—

1. *Fergusonite* from Greenland. A very rare mineral, crystallised: sp. gr. = 5.577.

2. Brown yttrotantalite from Ytterby: sp. gr.,  $a = 5.056$ ;  $b = 4.751$ ;  $c = 4.650$ .

3. Yellow yttrotantalite from Ytterby: sp. gr. 4.774.

4. Grey yttrotantalite from Gamle Kararfvet: sp. gr. = 4.306.

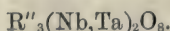
5. Tyrite from Helle, near Arendal: sp. gr. = 4.767 – 4.858.

6. Bragite from the same locality: sp. gr. = 5.267.

All these substances agree in changing their colour to yellow or greenish when heated.

	1.	2.			3.
		<i>a.</i>	<i>b.</i>	<i>c.</i>	
Ta <sub>2</sub> O <sub>5</sub> .....	6.30	8.73	9.53	49.85	27.04
Nb <sub>2</sub> O <sub>5</sub> .....	44.45	40.16	39.93		28.14
SnO <sub>2</sub> .....	0.47	0.91	0.23	—	—
WO <sub>3</sub> .....	0.15		0.21	—	—
YO.....	24.87	38.26	26.25	38.01	24.45
ErO.....	9.81		11.79		8.26
CeO.....	2.00	—	1.79	—	—
La(Di)O.....	5.63	—	—	—	—
CaO.....	0.61	3.40	3.04	3.29	4.17
UO.....	2.58	1.98	1.20	2.91	2.13
Fe(Mn)O.....	0.74	3.09	0.60		0.72
H <sub>2</sub> O.....	1.49	4.47	5.20	6.19	5.12
	99.10	101.00	99.77	100.25	100.03
	4.	5.		6.	
		<i>a.</i>	<i>b.</i>		
Ta <sub>2</sub> O <sub>5</sub> .....	43.44	—	—	—	2.04
Nb <sub>2</sub> O <sub>5</sub> .....	14.41	45.82	45.60	—	43.36
SnO <sub>2</sub> .....	—	0.45	0.45	—	0.83
WO <sub>3</sub> .....	—	—	—	—	—
YO.....	28.81	18.69	22.31	—	22.68
ErO.....	1.73	11.71	13.97	—	13.95
CeO.....	0.47	5.70	3.03	}	3.33
La(Di)O.....	—	3.56	1.51		
CaO.....	—	2.39	2.05	—	1.93
UO.....	1.56	6.21	5.38	—	8.16
Fe(Mn)O.....	1.51	1.50	0.82	—	—
H <sub>2</sub> O.....	7.14	4.88	4.88	—	4.18
	99.07	100.91	100.	—	100.46

On calculating these analyses, we obtain the general result that  $R'' : (Ta, Nb)$  is equal to 3 : 2 atoms. All these substances may therefore be expressed by the general formula—



They differ only in the quantities of isomorphous elements, Ta, Nb — Y, Er, Ce, U, Fe, Ca.

Fergusonite is distinguished by its crystalline form (tetragonal and hemihedral), but the same form has been found in yttrotantalite and tyrite.

Water cannot be regarded as a primitive and essential constituent, for the mineral from Greenland, which is least changed of all, contains only a small portion, and the proportion of water in the others is very variable.

#### IV. *Polycrase and Euxenite.*

These two Norwegian minerals were discovered by Scheerer. Polycrase occurs in rhombic crystals; euxenite is known only massive.

1. Crystallised polycrase from Hitterö: sp. gr. = 5.12.
2. Massive polycrase from Hitterö: sp. gr. = 4.972.
3. Euxenite from Alvö (Arendal): sp. gr. = 4.984 — 5.007.
4. Euxenite from Mörefjär (Arendal): sp. gr. = 4.672.
5. Euxenite from Eydland (Lindesnäs): sp. gr. = 5.058 — 5.103.

	1.	2.	3.	4.	5.
Ta <sub>2</sub> O <sub>5</sub> .....	4.00	—	—	—	—
Nb <sub>2</sub> O <sub>5</sub> .....	20.35	25.16	35.09	34.59	33.39
TiO <sub>2</sub> .....	26.59	29.09	21.16	23.49	20.03
YO .....	23.32	23.62	27.48	16.63	14.60
ErO .....	7.53	8.84	3.40	9.06	7.30
CeO .....	2.61	2.94	3.17	2.26	3.50
CaO .....	—	—	—	—	1.36
UO .....	7.70	5.62	4.78	8.55	12.12
FeO .....	2.72	0.45	1.38	3.49	3.25
K <sub>2</sub> O .....	—	—	—	—	0.82
H <sub>2</sub> O .....	4.02	3.00	2.63	3.47	2.40
	98.84	98.72	99.09	101.54	98.77

Both minerals contain isomorphous niobates and titanates of normal composition. They differ only in the proportion of these constituents—



Like fergusonite, &c., they give very different amounts of water;

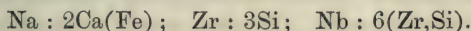
but the water is, in my opinion, not a primitive and essential constituent of these minerals.

### V. *Woehlerite*.

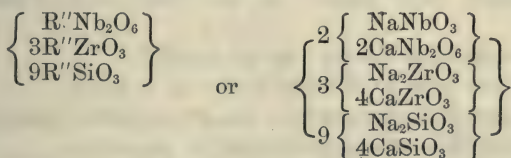
A yellow or reddish mineral from the zircon-syenite of Brevig, in Norway, where it was detected by Scheerer. It fuses before the blowpipe, and is decomposed by hydrochloric acid, the insoluble part being a mixture of silicic and niobic acids, while zirconic acid, lime, and soda are dissolved. Repeating the former analyses of Scheerer and Hermann, I have obtained—

Niobic acid .....	14.41
Silicic acid .....	28.43
Zirconic acid .....	19.63
Lime .....	26.18
Protoxide of iron .....	2.50
Soda .....	7.78
	<hr/>
	98.93

Hence follow the atomic ratios—



By changing  $2\text{Na}$  into  $\text{R}''$ , the ratio of  $\text{R}'' : (\text{Nb}, \text{Si}, \text{Zr})$  is  $1 : 1, 1$ . I therefore propose the simple formulæ—



The crystals of woehlerite are rhombic, the primitive vertical prism being of  $90^\circ 16'$ , according to the observations of Des Cloizeaux.

### VI. *Pyrochlore*.

Pyrochlore was found in the zircon-syenite of Fredriksvärn and Brevig, in the southern part of Norway. Then it was detected near Miask, in the Ural mountains, and more recently in the Kaiserstuhl, a small group of doleritic mountains between the Rhine and Freiburg, in Baden. It is mostly crystallised; the crystals are regular octahedrons.

The history of the chemical investigation of pyrochlore is very remarkable, on account of the great differences in the analyses, not only of different investigators, but also of the same chemists who have endeavoured to determine the elements of this interesting mineral.



Woehler at first declared the pyrochlore from Fredriksvärn to be a titanate of calcium, cerium, uranium, and iron, but seven years after he found a considerable amount of tantalic acid. On examining the pyrochlore of Miask, Woehler obtained the same elements, moreover sodium, fluorine, and thorium, but no uranium, while the pyrochlore of Brevig, much resembling that of Fredriksvärn, gave also thorium, but could not be completely investigated.

The pyrochlore of Miask was analysed by Hermann in the years 1844, 1850, and 1869, but the three analyses published by him differ considerably. They gave, *i.e.*—

	1.	2.	3.
Thoric acid .....	0	0	8·88 per cent.
Zirconic acid .....	5·57	0	0 „
Oxides of Ce, La ....	5·32	15·23	6·20 „

It is evident that these analyses left many doubts on the true composition of pyrochlore. I therefore endeavoured in my own analyses to separate the constituents by the best methods, and to verify the results by investigating the single substances.

The metallic acids of pyrochlore are niobic, titanic, and thoric acid. I never found zirconic acid. Thorium occurs solely in the pyrochlore of Miask and Brevig; titanium in all varieties except the pyrochlore of Kaiserstuhl.

1. Pyrochlore from Miask: sp. gr. 4·35 — 4·37. Mean of four analyses.

2. Pyrochlore from Brevig: sp. gr. = 4·22.

3. Pyrochlore from Fredriksvärn: sp. gr. = 4·228.

4. Pyrochlore from Kaiserstuhl: sp. gr. = 4·563; analysed by Prof. Knop of Carlsruhe, and communicated to the author.

	1.	2.	3.	4.
Nb <sub>2</sub> O <sub>5</sub> .....	53·19	58·27	47·13	58·62
TiO <sub>2</sub> .....	10·47	5·38	13·52	—
ThO <sub>2</sub> .....	7·56	4·96	—	—
CeO* .....	7·00	5·50	7·30	9·56†
CaO .....	14·21	10·93	15·94	15·15
MgO .....	0·22	—	0·19	—
FeO .....	1·84	5·53	10·03	2·09
UO .....	—			
Na .....	3·71	3·94	3·12	8·60‡
Fl .....	(3·06)§	3·75	2·90	(5·98)
H <sub>2</sub> O .....	—	1·53	1·39	—
	101·26	99·79	101·52	100·

\* Including La, Di. † I found in that variety 62·46 Nb<sub>2</sub>O<sub>5</sub> 6·69, CeO 3·00 (La, Di)O.

‡ 5·28 Na, and 3·32 K.

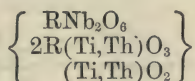
§ Woehler found 3·43 per cent.

If  $R''$  designs Ce, Ca, U, Fe, the following formulæ may be deduced from the analyses:—

Miask. Brevig. (1. 2.)	Fredriksvärn. (3.)	Kaiserstuhl. (4.)
$\left\{ \begin{array}{l} m \text{ RNb}_2\text{O}_6 \\ n \text{ R(Ti,Th)O}_3 \\ o \text{ NaFl} \end{array} \right\}$	$\left\{ \begin{array}{l} \text{R}_2\text{Nb}_2\text{O}_7 \\ \text{RTiO}_3 \\ \text{NaFl} \end{array} \right\}$	$\left\{ \begin{array}{l} 3\text{R}_2\text{Nb}_2\text{O}_7 \\ 5(\text{Na,K)Fl} \end{array} \right\}$
1. $m = 5$ $n = 4$ $o = 4$ .		
2. $m = 5$ $n = 2$ $o = 4$ .		

While the molecules  $\text{RNb}_2\text{O}_6$  and  $\text{RR}^{\text{iv}}\text{O}_3$  must be considered as isomorphous, according to the experiments on the foregoing niobates, we find in the two varieties 3 and 4, a basic niobate. Now it is shown by Marignac, that the double fluorides  $\text{R}''\text{R}^{\text{iv}}\text{Fl}_6$  are isomorphous with  $\text{R}''\text{WO}_2\text{Fl}_4$  and  $\text{R}''\text{NbOFl}_5$ ; it may therefore be supposed that the corresponding oxysalts  $\text{R}''\text{R}^{\text{iv}}\text{O}_3$  and  $\text{R}''_2\text{Nb}_2\text{O}_7$  may also be capable of assuming the same form.

There are still two minerals, containing tantalum or niobium, which I have not myself had the opportunity of analysing, namely, samarskite and aeschynite. Aeschynite has, however, been the object of researches by Marignac, who has pointed out that it is a mixture of niobates, titanates, and thorates of Ce, La, Ca, and Fe, leading to the formulæ—



On comparing the composition of the natural tantalates and niobates as far as possible with their crystalline forms, it will soon be understood that there are several interesting series of isomorphous and heteromorphous bodies.

#### A. Isomorphous Groups of the Rhombic System.

	Ratio of the axes.	
	a.	c.
Tantalite, Niobite .....	0.82	: 0.82
Wolfram .....	0.83	: 0.87
Tantalie acid.....	0.83	: 0.82
Wolframic acid .....	0.83	: 0.87
Titanic acid (Brookite) .....	0.84	: 0.94
Polycrase (Euxenite) .....	0.94	: 0.91
Aeschynite .....	0.49	: 0.67
Woehlerite .....	0.99	: 0.75
Broncite ( $\text{MgSiO}_3$ ).....	1.03	: 1.18

*B. Isomorphous Groups of the Quadratic System.*

	<i>e.</i>
Tapiolite .....	0·64
Titanic acid (Rutile) .....	0·64
Zircon ((Zr,Si)O <sub>2</sub> ) .....	0·64
Tin ore (SnO <sub>2</sub> ).....	0·67
Zirconic acid .....	1·00
Thoric acid .....	0·16
Xenotime (Y <sub>3</sub> P <sub>2</sub> O <sub>8</sub> ).....	0·62
Fergusonite .....	1·50
Scheelite (CaWO <sub>4</sub> ) .....	1·53
Scheelbleierz (PbWO <sub>4</sub> ) .....	1·57
Gelbbleierz (PbMoO <sub>4</sub> ).....	1·58

We must therefore assume—

1. The molecules RTa<sub>2</sub>O<sub>6</sub>, RWO<sub>4</sub>, RTiO<sub>3</sub> are isomorphous with the anhydrides Ta<sub>2</sub>O<sub>5</sub>, WO<sub>3</sub>, TiO<sub>2</sub>.

2. All these molecules are dimorphous. The regular form of pyrochlore is certainly also connected with the forms of its component minerals. We know that KFl and NaFl, like CaTiO<sub>3</sub> (perowskite) are regular, and that the same crystalline form is to be found in BaN<sub>2</sub>O<sub>6</sub>, SrN<sub>2</sub>O<sub>6</sub>, PbN<sub>2</sub>O<sub>6</sub>, which are analogous to RNb<sub>2</sub>O<sub>6</sub>.

The tantalates and niobates hitherto found in minerals are RNb<sub>2</sub>O<sub>6</sub>, R<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub>, R<sub>3</sub>Nb<sub>2</sub>O<sub>8</sub>, corresponding to the phosphates and arsenates.

VIII.—*Note on the Crystalline Principle of Barbadoes Aloes.*

By WILLIAM A. TILDEN, D.Sc. Lond.

THIS substance was examined some years ago by Dr. Stenhouse, who analysed it and a bromo-derivative.

After several unsuccessful trials, I have obtained from it a chloro-substitute, corresponding to the brominated body already known. It is only necessary to treat the aloin with excess of chlorine in the presence of concentrated hydrochloric acid. This is most conveniently done by the method adopted by Stenhouse in preparing the chlorinated derivatives of orcin.

Some powdered potassic chlorate was introduced into a quantity of ordinary fuming hydrochloric acid. The crystallised aloin to be operated upon was dissolved in another portion of the same acid, and the solution so obtained, when quite cold, was poured gradually and with



constant agitation into the mixture of hydrochloric acid and chlorate. After each addition of the aloin, a red coloration was produced, but this instantly disappeared, the solution assuming a clear orange colour, and depositing in a few minutes a copious crop of yellow granules, the quantity of which increased by standing for a few hours. It was then filtered off, washed with a little water, and crystallised from warm rectified spirit. The tufts of bright yellow prisms which were deposited in a few hours were collected and dried by exposure to dry air. They bear, without change of colour or general appearance, a temperature of  $120^{\circ}\text{C}$ ., and even much higher. At  $120^{\circ}$  they lost weight in one experiment to the extent of 10·86, in another 10·04 per cent.

·237 gram gave by boiling with nitric acid and nitrate of silver, ·216 of chloride of silver, corresponding to 22·53 per cent. of chlorine.

The formula  $\text{C}_{17}\text{H}_{15}\text{Cl}_3\text{O}_7 \cdot 3\text{H}_2\text{O}$  requires 10·99 per cent. of water, and 21·66 per cent. of chlorine.

The proportion of chlorine found being thus a little too high, the substance was recrystallised and carefully washed. This time it was dried at  $120^{\circ}$  previous to analysis.

I. ·247 gram gave ·251 of chloride of silver.

II. ·1835 gram, by combustion with a mixture of lead chromate and potassic dichromate, gave ·062  $\text{H}_2\text{O}$  and ·304  $\text{CO}_2$ .

	Theory.		Experiment.	
			I.	II.
$\text{C}_{17}$ .....	204	46·62	—	45·17
$\text{H}_{15}$ .....	15	3·42	—	3·70
$\text{Cl}_3$ .....	106·5	24·34	25·13	—
$\text{O}_7$ .....	112	—	—	—

Again, therefore, the chlorine is rather above, and the carbon below the theoretical numbers, although they are sufficiently near to leave no doubt as to the identity of the body. I think it probable, therefore, that notwithstanding that the crystals are to all appearance clean, and when dissolved in water, give no trace of turbidity with nitrate of silver, they are contaminated with a small quantity of another similar body, containing a higher percentage of chlorine.

This chloraloin is more soluble in water than the corresponding compound containing bromine, and differs from the original aloin in its comparative stability. Thus, although very soluble in aqueous ammonia, it will crystallise out but little altered when the ammonia is allowed to evaporate, and it may be dissolved in ordinary nitric acid (sp. gr. 1·37), without change of colour.

The aloin from which this body is derived, when acted upon by nitric acid, yields, besides oxalic and picric acids, rather more than

30 per cent. of its weight of chrysammic acid; and in fact I find it a more convenient source of chrysammic acid than crude aloes. But the chlorinated compound, boiled with nitric acid and nitrate of silver, furnishes oxalic and picric acids only, without a trace of either aloetic or chrysammic acid.

In most of the reactions of aloin and its chloro- and bromo-derivatives, there is such a marked parallel with those of the orcins, that I think it worth while to submit them to a further examination.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
BRITISH AND FOREIGN JOURNALS.

Physical Chemistry.

**On Electrolysis and Conduction of Electricity through Liquids.** By G. QUINCKE (Pogg. Ann. cxliv, 1—33 and 161—190).

THE author commences by developing some formulæ for the force of the electrical current to decompose a compound liquid.

Suppose the electrolyte be an aqueous solution of sodium chloride enclosed in a straight tube, and that, by the passage of a current, the particles of the liquid are thrown into a state of tension: the component atoms of chlorine and of sodium then receive charges of free electricity, which, as they need not be equal in sign and in quantity, may be called  $\epsilon$  and  $\epsilon'$ . The accelerating forces acting upon  $\epsilon$  and  $\epsilon'$  at a certain point are expressed by—

$$-\frac{dV}{dx} \epsilon \text{ and } -\frac{dV}{dx} \epsilon'.$$

where  $V$  denotes the potential of the free electricity at this point and the force is reckoned as positive in the direction of the positive  $x$ , the charges  $\epsilon$  and  $\epsilon'$  carrying as a rule the particles to which they are attached along with them, soon attain, on account of the friction of the moving particles against one another, the constant velocities

$$v = -C \frac{dV}{dx} \epsilon, \text{ and } v' = -C' \frac{dV}{dx} \epsilon',$$

where  $C$  and  $C'$  are constants depending upon the quantity of mass to be moved, upon the friction between the particles and upon the force with which  $\epsilon$  and  $\epsilon'$  are retained by the moving atoms. The force separating the chlorine from the sodium atoms is evidently proportional to their mean relative velocity, and is expressed by

$$K = A(v - v') = -\frac{dV}{dx} (B\epsilon - B'\epsilon').$$

where  $A$  and  $B = AC$  are constants.

If  $q$  represent the section of the electrolysed liquid,  $\lambda$  its conductivity, and  $i$  the current intensity, we get—

$$\frac{dV}{dx} = -\frac{i}{\lambda q} \text{ and } K = \frac{i}{q} \frac{B\epsilon - B'\epsilon'}{\lambda}.$$

from which it appears that the force tending to separate the constituents of an electrolyte is proportional to the density of the current, that is the strength of the current per unit of sectional area of the electro-



lyte. As long as this force is too small to overcome the chemical affinity, the liquid will behave as an insulator, but it may become conducting by an increase of the density of the current.

Having shown the leading conceptions upon which the author bases the mathematical treatment of the subject, we shall now give shortly his theoretical results:—

1. The force tending to separate the ions increases with the electromotive force of the battery used, and is inversely proportional to the length, but independent of the section and of the conductivity of the liquid, supposing the resistance of the rest of the circuit to be negligible in comparison with that of the electrolyte.

2. The quantity of the ions separated is proportional to the mean relative velocity with which they pass one another.

3. According as the constituents of an electrolyte both approach to or recede from an electrode, or as they move with different velocities in opposite directions, the concentration of the liquid at this electrode will increase or decrease.

By his first series of experiments, the author proves that electrolytes obey the same laws of conduction as metallic conductors. An apparent exception to Ohm's law was shown to be none. It had been observed that when part of a conducting wire of platinum or of German silver was surrounded by dilute sulphuric acid, its resistance was not appreciably diminished, as, according to the laws of derived currents, it ought to be. The author ascribing these irregularities merely to polarisation taking place at the terminals of the platinum wire, took a copper wire immersed in cupric sulphate and found that by increasing the section of the surrounding liquid, he could diminish the resistance of the circuit, thus proving that part indeed of the current had passed through the liquid, as it is required by the law of derived currents.

On examining the distribution of the free electricity in the circuit, the tension at the two poles was scarcely ever found to be equal, being greater sometimes at the positive, sometimes at the negative pole.

The same was observed when the current was made to pass through a column of distilled water between two platinum plates which were connected with the poles of the battery. The tension on the two plates as examined by a condenser and a Dellmann's torsion balance, was found to be different, whilst their electrical difference remained constant, even when the length of the intervening column of water was considerably diminished.

Inasmuch as the resistance of the water, even on approaching the plates, remained still very great as compared with the internal resistance of the battery, the constancy of the electrical difference of the plates could be predicted from theory.

The author determined also the electrical difference between two points in the interior of a column of distilled water between two platinum plates which were connected with the poles of the battery. The distance of these two points being only about one-fourth of the distance between the plates, their electric difference was accordingly found to be considerably less. In this case also the tension at the two points was found to be somewhat different, in the proportion of 2·854 to 3·47 and 2·9 to 3·25.

The author found his results confirmed on repeating his measurements with Sir W. Thomson's quadrant electrometer, which he considers a far more trustworthy and practical instrument than Dellmann's torsion balance.

Next the current was passed through copper electrodes into a solution of cupric sulphate, and afterwards the cupric sulphate was replaced by a metallic conductor of the same resistance. It was found that the tension at the electrodes was in both cases the same, thus showing that the distribution of the free electricity in a metallic connection is not altered, when part of it is replaced by an electrolyte of the same resistance.

The author then discusses the point why even the weakest electric forces are capable of producing a certain amount of current and decomposition gradually increasing with the intensity of the force, whilst according to theory, current and electrolysis ought to set in suddenly and strongly as soon as, and not before, the tension has come to a certain height.

He points out that the electrolysis of certain substances can probably be effected only by the current obtained on discharging a Leyden jar.

In order to examine the action of a current in the interior of an electrolyte, a trough filled with solution of cupric sulphate was divided by a mica plate into two compartments, communicating with each other through a hole of 0.2 mm. diameter in the middle of the plate.

Although of course the current, entering and leaving the liquid through two copper plates, was considerably increased in density during its passage through the hole, no decomposition took place in its neighbourhood, and some gas bubbles, which indeed were observed to rise at both sides of the hole, turned out to be nothing but air expelled by the rise of temperature due to the contraction of the current.

On illuminating the liquid strongly, certain undulatory movements could be observed in the neighbourhood of the hole, probably caused by the different portions of the liquid becoming unequally heated.

When, as is almost always the case, the concentration of the liquid decreases in the neighbourhood of the electrodes, it must be concluded that  $\epsilon$  and  $\epsilon'$  have opposite signs. But in the electrolysis of solutions of  $2\text{Cd}$ ,  $\text{Cl}_2\text{Cd}$ ,  $\text{Cl}_2\text{Zn}$ ,  $\text{I}_2\text{Zn}$ , where the concentration increases near the anode,  $\epsilon$  and  $\epsilon'$  appear to have both the negative sign. Notwithstanding this exceptional behaviour, a solution of iodide of cadmium, traversed by the current, was found to have no other effect on the distribution of free electricity in the circuit than an ordinary electrolyte or metallic conductor of the same resistance.

It was further established that the intensity of the current, whilst passing through a solution of this salt, is the same as in the metallic part of the circuit.

R. S.

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**On Electric Conduction by Liquids without Electrolysis.** By P. A. FAVRE (Compt. rend., lxxiii, 1463—1467).

IN spite of the labours of Faraday and Foucault, and in spite of their argument, says M. Favre, physicists are generally slow to admit true



electric conduction in liquids, as distinct from electrolytic transference. For, while it cannot be denied that a current may be transmitted through a liquid without visibly electrolysing it, it is explained that in these circumstances electrolysis is really taking place, though it cannot be seen. M. Favre has experimented on the subject under conditions in which electrolysis was impossible.

He first examined the gases obtained from the voltameter in the case just referred to, where electrolysis really takes place, though not apparently. The liquid in the electrolytic cell having become thoroughly charged with oxygen, the hydrogen that is given off at the cathode is burned up as it is produced, while the oxygen set free at the anode goes to replace that which is used up in burning the hydrogen. He gives a table showing the amount of gas given off in a certain time, and under conditions stated, and the composition of it; also the quantity and the composition of the gas absorbed by the liquid of the cell. The battery used was that of Smee, which, though not constant, he found convenient, because, by collecting the hydrogen eliminated during its action, he had an electro-chemical measure of the quantity of electricity that had been passing in the circuit, and one which is easily compared with the indications of the voltameter. A powerful rheostat was also used, when required, to diminish the current.

The following experiments were then made. The voltameter, just as it was, containing the liquid in which large quantities of oxygen and hydrogen were dissolved, was joined up with *two* Smee's cells; and these cells, which for four and twenty hours previously had not given off a single bubble of gas, the circuit being open, now gave, each of them, 20 cubic centimeters in that time. Not a trace of gas was obtained from the voltameter. The acid liquid of the voltameter was now replaced by a similar liquid, which had been boiled so as to expel all the dissolved gases, the voltameter, together with its delivering tube, being completely filled with the boiling liquid. A perfectly similar result was obtained, except that the gas given off by the Smee's cells was rather less in quantity. On replacing one of the Smee's elements by a Daniell's cell, and repeating the experiment, a quantity of copper was deposited in the latter, which corresponded to the gas given off by the Smee in circuit; but no gas came from the voltameter, and when solution of cupric sulphate was substituted as an electrolyte for the dilute sulphuric acid, which had previously been employed, it was found that after four days, though a deposit of copper had occurred in the Daniell's cell, the negative plate of the voltameter did not exhibit a trace of it.

From these experiments Favre argues for a true conduction, distinct from electrolytic transference, in liquids. For, according to his previous experiments (p. 1133 of last volume), not less than three Smee's cells, whose voltaic energy is expressed by the number 15,000 per cell in units of heat for a certain amount of chemical decomposition, would be required to effect the electrolysis of the acid liquor of the voltameter, in which, for a similar amount of decomposition, about 45,000 units of heat are required.

J. T. B.



**Chemical Effects produced by the Heat of an Electric Discharge.** By M. BECQUEREL (*Compt. rend.* lxxiv, 83—87).

THE electric spark is caused by the incandescence of the particles in the path of the discharge. Each particle may thus be considered as momentarily under the influence of a concentration of intense heat, which is capable of producing, not only chemical combination, but also all the effects of fusion and reduction obtainable by purely chemical means.

Becquerel has experimented on these effects, but instead of employing a very powerful battery, as Davy did, he used an induction coil of moderate power, and sometimes increased the temperature due to the discharge by adding heat got from a blow-pipe, and from the burning of powdered charcoal at the place where the discharge is taking place.

To obtain the highest possible temperature the surface over which the heat is distributed must be as small as possible. The discharge was, therefore, taken from a finely pointed platinum wire, and the substance operated on was generally placed on a little platinum plate about a square centimeter in surface. The intensest heat was at the point of the platinum wire, and this formed the negative electrode. Sometimes, as in the reduction of a volatile metal, two pointed platinum wires were employed, and were brought together at the bottom of a U-tube, in which the substance to be reduced was contained. When cinnabar is thus treated, the interior of the tube becomes coated with metallic mercury.

The oxides of silver, lead, tin, and copper, were reduced by mixing them with powdered charcoal, and treating them in the U-tube as above. The oxides of nickel, cobalt, chromium, iron, &c., were reduced in like manner with the aid of charcoal powder obtained from sugar.

By means of the heat of the discharge, the fusion of silica and alumina, and other earthy materials, was also effected. The melted portions were obtained in little round grains, which, when they were broken up and examined with a microscope and Nicol's prism, sometimes exhibited the appearance of doubly refracting crystals. The crystals were evidently formed by the somewhat slow cooling of the interior portions of a little melted mass. Crystals of silica were obtained, both white and coloured with cobalt. It was not, however, proved that they were true crystals of quartz. Alumina crystals were also obtained, both white, and coloured with chromium and iron. Similar colours, blue, red, green, and yellow, were given by each metal, which corresponds with the observation that the colours in corundum appear to be due sometimes to iron and sometimes to chromium.

Becquerel in his paper compares the results of his experiments with the effects of lightning in forming the vitreous layers observed on the tops of mountains. He thinks that the metallic iron, and sulphide of iron, which have been found on the surfaces of rocks and on trees, are due to lightning, which both effects the transport of materials, and acts, sometimes as a reducing agent, sometimes as an agent to produce chemical combination.

He concludes by asking whether the results described are solely due

to heat, and he believes that such is not the case. Probably they are due partly to heat and partly to electro-chemical action; for whenever an electric discharge takes place through a compound body, it is accompanied by a tendency to chemical decomposition, and by a power of transferring the elements in opposite directions.

J. T. B.

**On a Relation between Capillary Action and Density in Saline Solutions.** By C. ALPH. VALSON (*Compt. rend.*, lxxiv, 103).

VALSON describes experiments on the height of the capillary column of various saline solutions in a glass tube of half a millimeter section. He took *normal*\* solutions of the different salts, and determined the density of the solution and the height of the capillary column, and came to the conclusion that the product of the height and density is constant.

The salts which he examined were the soluble chlorides, bromides, iodides, sulphates, and nitrates of the alkalis and alkaline earths, also of magnesium, zinc, cadmium, lead, and silver. The densities of the normal solutions of these salts range from 1.023, for lithium chloride, to 1.133, for silver nitrate, and the height of the capillary columns from 60.8 mm. to 54.2. With two or three exceptions, the products  $D \times H$  (where  $D$  stands for the density, and  $H$  for the height of the column) lay between the numbers 61.5 and 62.0.

He also deduces the following formula, which gives the capillary height in millimeters in terms of the density of a saline solution;— $H = 118.5 - 56.8 \times D$ . This he finds to hold good between wide limits as to density, and he shows that, in passing from a normal solution to any other the increase of height is proportional to the diminution of the density.

J. T. B.

**The State of Substances in Solution.** By M. BERTHELOT (*Compt. rend.*, lxxiii, 1472—1474; lxxiv, 48—52, and 119—122).

**I. Metallic Salts.**—The researches detailed by Berthelot in these papers form a continuation of his thermochemical examination of the ammoniacal salts (*Compt. rend.*, lxxiii, 745 and 864; *Journ. Chem. Soc.*, Dec. 1871, 1128). The investigations are now extended to the case of metallic salts formed by the union of acids with the oxides of zinc, copper, lead, &c., and particularly with ferric oxide, and were undertaken chiefly with a view of determining under what conditions double decomposition takes place when solutions of these salts are mixed. In studying the subject he takes advantage of a theorem which may be

\* That is, solutions in which an equivalent of each salt in grams is dissolved in a litre of water. This is somewhat misleading, for there is no mysterious connection between the atomic weights and the results obtained; and it would have been more satisfactory had the observations been pushed up to a high density, such as 1.6, obtainable by mixing sulphate of zinc and sulphate of copper in the same solution, instead of stopping at 1.13, which is that of the *normal* solution of silver nitrate. The general result which M. Valson's numbers show, though he does not state it in his paper, is, that so far as these difficult experiments can be relied on, the *surface tension of water is not affected by the presence of the salts dissolved.*—J. T. B.



stated as follows:—If  $N$  and  $N_1$  be respectively the quantities of heat given off during the union of a certain base with each of two acids, the combination taking place in presence of a definite quantity of water, and if  $N'$   $N_1'$  be the quantities of heat disengaged under similar conditions by the union of another base with the same acids, then whenever the quantity,  $N - N_1 - (N' - N_1')$ , is not too small to be measured, if any double decomposition occurs when solutions of these salts are mixed, it can be detected, and the amount of it determined. He also makes use of the following important result of his experiments, that the heat given out in the formation of metallic salts varies with the quantity of water present. That being the case, he was generally able to make  $N - N_1 - (N' - N_1')$  different from zero, for if it be zero for solutions of the salts in a certain volume of water, it ceases to be zero when solutions more concentrated or more dilute are employed.

In the case of many of the salts of the metals just mentioned, the concentration of the solution exerts a far greater influence on the quantity of heat disengaged during a reaction than it does in the case of salts of the alkalis. Thus equivalent quantities of—

	Heat-units.
Zinc acetate (1 eq. in grams in 10 litres) and caustic potash (1 eq. in 2 litres) being mixed, gave . . . .	+ 4.40*
Zinc acetate (1 eq. in 2 litres) and caustic potash (1 eq. in 10 litres) . . . . .	+ 5.40

This effect is almost entirely due to the difference in concentration of the zinc acetate: for if a solution of caustic potash, one equivalent in two litres, be diluted with water so as to become ten litres, the thermal effect is scarcely appreciable, neither is the effect of the dilution of an alkaline acetate more perceptible. On the other hand, solution of zinc acetate, 1 equivalent in 2 litres

diluted to 4 litres, gives 0.50 heat-units.

“ 10 “ 1.01 “

Experiments were also made on the heat developed during the solution of zinc oxide in acetic acid in presence of different quantities of water, and the heat developed was found to increase as the solution is diluted. Analogous results were obtained with many other salts. In some cases, however, as in those of the acetates of potassium and sodium, and in that of zinc sulphate, after a certain point is reached, the addition of water has little or no effect.

The preliminary numbers being determined, Berthelot proceeded to ascertain, by observing the heat developed on mixing solutions of various salts, when double decomposition takes place. Thus, he mixed zinc acetate with sodium sulphate, and again zinc sulphate with sodium acetate, and showed that in the former case the heat given out is nothing more than that due to the dilution of the zinc acetate, while in the latter the occurrence of double decomposition must be supposed, in

\* It is not stated in this or in either of the previous papers what the unit of heat is, or how the experiments were made. It appears to be about 1,000 times that ordinarily employed, which would correspond to the quantity of heat required to raise 1 litre of water through 1°.



order to account for its development.\* Experimenting thus, he shows that on mixing two solutions of salts, the final result is that the most powerful base unites with the most powerful acid, and the weaker base with the weaker acid; in fact, that salts, are formed in the order of their stability, double decomposition occurring when necessary for this final result. This was shown to hold for various salts of several metals, but the most striking results were obtained in the case of ferric salts.

II and III. *Ferric Salts*.—The sulphate, nitrate, and acetate were prepared with great care, and were examined, each salt first by itself in solutions of varied concentration, and then in mixture with solutions of other salts. By means of the heat given out during dilution and mixture, Berthelot was able to examine very particularly the state of the union which exists between the acid and base in solutions of ferric salts. The instability, or at least the feebleness, of the union was first pointed out by Péan de St. Gilles in the case of the acetate. Solutions of the salts: first, recently dissolved; secondly, recently dissolved but boiled for some minutes and then cooled; and, thirdly, after the solution had been kept for three months,—were mixed with equivalent solutions of caustic potash, and the following results were obtained:—In the case of the sulphate, the heat developed in all three cases was nearly the same; but in the case of the nitrate, while the solution of the salt recently dissolved in the cold was sensibly unchanged by boiling, the same solution kept for three months gave a result which proved that slow disunion between the base and the acid had been going on. The acetate was also found to be slightly decomposed when the solution is kept for a long time, but when it is boiled for a few minutes the acid and base are found to be almost completely disunited.

The effect of ebullition on ferric acetate was carefully examined, and also that of adding subsequently solution of potassium sulphate (according to Péan de St. Gilles); and a secondary disengagement of heat that was observed showed a molecular coagulation or condensation, which appears to correspond with the assumption of the insoluble state in which the oxide is found after this kind of precipitation. The effect of long keeping, and of diluting the solution of the salt with a large volume of water was also examined. The following are the general results of the investigation:—

In solutions of ferric salts the oxide and the acid are united in an incomplete and feeble manner, and the union is affected by the water of the solution, and greatly by temperature. This is most apparent in the case of salts formed with the weaker acids. The reaction of the water in breaking up the salt is not instantaneous, but progressive, as is the case with the decomposition of ethers by water; and finally the effects are not always reversible by reversing the conditions, for the oxide of iron once separated from its acid assumes a molecular condition which prevents it from returning to its old state in combination.

\* I speak here of *heat developed*; but it must of course be understood, as shown by the numbers, which want of space does not permit me to quote, that cold is often produced. This, according to the ordinary extension of language, is spoken of as development of a negative quantity of heat.—J. T. B.

The action of an acid on its corresponding ferric salt was examined, and heat was shown to be liberated in the case of the nitrate and sulphate when the acid solution is added, which indicates an increased union between the oxide and the acid, due to the presence of free acid. A solution of an alkaline salt of the same acid does not produce much effect on the solution of the ferric nitrate or sulphate, but when solution of sodium acetate is mixed with solution of ferric acetate, complete though gradual decomposition takes place.

The presence of two ferric salts in a solution diminishes the decomposing power of water on each of them.

When a solution containing an equivalent of nitric acid is mixed with a solution containing an equivalent of ferric sulphate or ferric acetate, the sulphuric acid or the acetic acid is displaced by the nitric acid. Sulphuric acid completely displaces acetic acid from a ferric acetate.

Finally, when the double decompositions that take place on adding solutions containing various salts in equivalent quantities to solutions of ferric salts were examined, the rule, before established for the salts of zinc, copper, lead, &c., and for the ammoniacal salts, that the stronger acid joins itself to the stronger base, was completely established by the indications of the thermometer.

J. T. B.

### Affinity of Hydrogen for Chlorine, Oxygen, and Nitrogen.

By JULIUS THOMSEN (Deut. Chem. Ges. Ber., iv, 941—947).

IN connection with a forthcoming work on thermo-chemistry, the author has made some very careful determinations of the heat evolved or absorbed during the formation or decomposition of hydrochloric acid, water, and ammonia.

1. *Affinity of Hydrogen for Chlorine.*—This was determined by burning chlorine in an atmosphere of pure hydrogen, and estimating by analysis the amount of hydrochloric acid produced (12—15 grammes) after absorbing it in water. The gases and produced acid came in contact with nothing but glass and platinum. Special attention was paid to having the chlorine quite free from oxygen or chlorine oxides. There can be no doubt that Favre and Silbermann's determinations were made with chlorine containing oxygen (or hypochlorous acid), for they stored their chlorine over a solution, and it is almost certain that even in the dark chlorine slowly decomposes water.

Using Stas's atomic weights, the formation of the molecule of hydrochloric acid was found in four experiments to be attended with the following development of heat:—

21975	} Mean, 22001 heat-units = (H, Cl).
22018	
22003	
22008	

Using the ordinary atomic weights, the number of heat-units becomes 22007, which is practically the same.

The author has found the heat developed by the absorption of hydrochloric acid by water to be 17314 heat-units for HCl, Aq. The total

heat therefore evolved in the formation of aqueous hydrochloric acid is 39315 units for  $H, Cl, Aq$ .

The error in the former determinations of the heat of formation of hydrochloric acid, due to the presence of oxygen in the chlorine, has rendered all the other numbers which have been calculated from it inexact.

2. *The affinity of Hydrogen for Oxygen.*—The number of heat-units for  $H_2, O$  the author has found to be (using Stas's atomic weights) 68376. This number lies between that found by Andrews, and that by Favre and Silbermann.

3. *The affinity of Hydrogen for Nitrogen.*—This is best determined by the method adopted by Favre and Silbermann of decomposing solutions of ammonia by chlorine. The thermic phenomena may be thus analytically represented:—

$$(4NH_3Aq, 3Cl) = 3[(Cl, H, Aq) + (NH_3Aq, ClHAq)] - (N, H_3, Aq).$$

The author has found the development of heat for  $4NH_3Aq, 3Cl$  to be 119613 units; that for  $Cl, H, Aq$  is 39315 units; and that for  $NH_3Aq, ClHAq$  is 12270 units (*Deut. Chem. Ges. Ber.*, iv, 586); so that  $N, H_3, Aq = 154755 - 119613 = 35142$  units. The heat of absorption of ammonia by water the author has found to be 8435 units for  $NH_3, Aq$ , so that—

$$(N, H_3, Aq) - (NH_3, Aq) = (N, H_3) = 26707 \text{ units.}$$

Favre and Silbermann obtained for the reaction of chlorine on ammonia the number 129720 heat-units, which is 10107 greater than the author's. But they worked with the mercurial calorimeter, so that their determinations cannot claim much confidence. Had this error not been compensated by others it would have caused a great difference between the value of  $N, H_3$  as found by them and by the author. As it is, this value, according to Favre in 1868, is 25931 units, which is only 776 less than the author's number.

The above quantities taken together with that which the author has already determined for the latent heat of solution of sal-ammoniac contain the united thermic constants which have to be considered in the formation of sal ammoniac, as the following table shows:—

$(N, H_3)$	= 26707	= 11 × 2428	heat-units.
$(H, Cl)$	= 22001	= 9 × 2445	"
$(HCl, Aq)$	= 17314	= 7 × 2473	"
$(NH_3Aq, HClAq)$	= 12270	= 5 × 2454	"
$(NH_3, Aq)$	= 8435	= 5 × 2463	"
$(NH_4Cl, Aq)$	= 3882		
$(N, H_4, Cl)$	= 90609	= 37 × 2449	
$(H_2, O)$	= 68376	= 28 × 2442	

E. D.



**On the Alleged Influence of Calcination upon the Heat of Solution of Metallic Oxides.** By C. MARIIGNAC (Archives des Sciences [2], xlii, 209—220).

THE author criticises the results obtained by Ditte on the heat evolved by the solution of the oxides of zinc and magnesia in sulphuric acid. According to Ditte the heat evolved in these reactions increases in proportion to the temperature at which the oxide had been prepared (See this Journal, last volume, p. 793). Marignac, on carefully repeating these determinations, finds that the heat evolved by the oxides prepared at 350°—440°, at a dull red heat and at a bright red heat, is practically identical.

	MgO.	ZnO.
350° .....	—	261
440° .....	874	—
Dull red heat .....	875	266
Bright red heat ....	867	264

Marignac attributes the erroneous conclusions of Ditte to imperfections in the calorimetrical method which he employed.

T. E. T.

**On Change of Volume accompanying Solution.** By C. A. VALSON (Compt. rend., lxxiii, 1376—1379).

THIS paper is a continuation of the author's researches on the densities of saline solutions, noticed in our last volume (p. 987). A definite quantity of water (1 kilogram) is taken and a certain amount of any salt dissolved in it; the density of the salt itself being known, the volume of the solution is then determined and also the density of the solution. In all cases it is found that the volume of the solution of the salt is less than the sum of the volumes of the water and the undissolved salt. From these data it is easy to calculate the coefficient of contraction of each particular salt.

The author has made a series of experiments on various salts, some of the details of which, and the tables calculated therefrom, are given in the original paper. He has arrived at the following general conclusions:—

1. In every case there is a diminution in volume when an anhydrous salt is dissolved in water, that is, the volume of the solution is less than the sum of the volume of water and salt. Of all salts tried, ammonium chloride gives the least contraction.

2. The first portions of the anhydrous salt correspond to the maximum of contraction. As the strength of the solution increases, the contraction diminishes, until with very soluble salts, when the solution is nearly saturated the contraction is almost insensible.

3. Viewed with regard to their energy of contraction, the substances experimented on may be ranged in the following order, beginning with the greatest contraction: (a) with respect to the *non-metallic radicals*—carbonates, sulphates, chlorides, nitrates, iodides; (b) with respect to the *metals*—iron, zinc, copper, magnesium, strontium, barium, calcium, sodium, lead potassium, ammonium.

4. Hydrated salts give far less contraction than the corresponding anhydrous salts; the contraction is smaller as the number of molecules of water of crystallisation becomes greater.

5. Salts which crystallise in the anhydrous state are those in which the coefficient of contraction is smallest.

A. P.

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**On the Behaviour of Supersaturated Saline Solutions when exposed to the Open Air.** By CHARLES TOMLINSON (Proc. Roy. Soc., xx, 41—45).

FROM a series of painstaking experiments the author deduces the general conclusion, that supersaturated saline solutions, which would instantly solidify if exposed to the air of a room, may be kept for many hours in the open air of the country without crystallisation. Even newly sprouted leaves do not act as nuclei.

S. W.

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**A New Method of Preparing Supersaturated Solutions.** By L. C. DE COPPET (Compt. rend., lxxiii, 1324).

THE customary method of preparing a supersaturated solution consists in allowing a solution saturated at the boiling temperature to cool slowly, out of contact with atmospheric dust; the author has found, however, that it is possible to prepare supersaturated solutions of sodium sulphate by dissolving the *anhydrous* salt in *cold* water.

In order that the experiment may succeed, it is necessary to employ the anhydrous salt which has been heated to a temperature higher than 33° C., and cooled out of contact with air. This is easily effected by placing the salt in a glass tube, and having heated it to the required temperature, closing the open end until the contents have become cold.

The salt must be added to the water in small portions at a time, inasmuch as it becomes heated in contact with cold water, and the supersaturation may perhaps be due to this elevation of temperature. Cold water dissolves a quantity of anhydrous sulphate nearly five times as great as that which is contained, at the same temperature, in a saturated solution of the hydrate  $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$ .

According to the author's experience, a saturated solution of anhydrous sodium sulphate contains 35·8 per cent. of anhydrous salt at 14°, while a saturated solution of the 10-atom salt, at the same temperature, contains only 12·4 per cent. of anhydrous salt. Another experiment showed the solubility of the anhydrous sulphate to be 52·7 per cent. at 21° C, the solution of the hydrate,  $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$ , containing 20·9 parts of anhydrous salt. One fact, proved by many experiments, is that the crystallisation of a supersaturated solution of anhydrous sodium sulphate is always provoked by contact with a crystal of the salt containing 10 atoms of water, and it appears equally certain that the completely effloresced (anhydrous) salt exhibits the same property.

It seems, then, that the anhydrous sulphate which is obtained by

drying the decahydrated salt at a temperature below  $33^{\circ}$  C., cannot be identical with that which has been prepared at temperatures higher than  $33^{\circ}$ ; it is possible that they may be isomeric modifications. As regards the modification containing 7 molecules of water of crystallisation, not only does it not possess the above-mentioned property of determining the crystallisation of a supersaturated solution, but it is soluble to a considerable extent, even in the cold, in a solution already strongly supersaturated.

J. W.

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**On Liquid Transpiration and its Practical Use in Scientific and Technical Chemistry.** By LÖWENTHAL (*Zeitschrift für Anal. Chemie*, x, 298—305).

THE author employs an apparatus somewhat different from that used and described by Graham, to whose labours he often refers. The vessel containing condensed air he makes of a capacity of not less than 1,500 cub. cent.; he uses two capillary tubes, with two stopcocks, made of exactly equal dimensions, so that two experiments may be carried on simultaneously. Instead of placing the tubes in water at a known temperature, the author finds it easier to regulate the temperature of the room so that it shall be maintained at a constant point during the experiments. The tubes used are of varying capacity, containing from 2.5 to 57 cub. cent., some of these having one and some two bulbs. The time which the liquid takes to pass through the capillary tube is noted by a method similar to that employed by Graham in his experiments.

The author has shown that the fatty oils used in the arts have very different rates of transpiration, and that this is also the case with milk, beer, wine made from fruits, grape-wine, and various other substances. This fact, he suggests, may be turned to practical account in testing such compounds.

He shows further that, for at least some liquids, there exists a relation between their respective diffusion and transpiration rates. Thus, Graham gives the diffusion of HCl solution to NaCl solution as 1:0.7, the author has found their respective rates of transpiration to be as 1:0.732. So the diffusion of NaCl to sugar is as 2.33:7, their transpiration rates as 2.33:5.83.

M. M. P. M.

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**On the Sounds of Vibrating Flames.** By M. BALLO (*Deut. Chem. Ges. Ber.*, iv, 906).

A PETROLEUM lamp chimney is supported in a horizontal position by a clamp, and the tapering upper portion covered over with a cylinder of tin plate; a perforated cork is fixed in the other end and a stream of coal-gas thus passed through and inflamed at the end covered with tin. A jet of oxygen issuing from a drawn-out glass tube is then brought to the flame and passed through it, so that a jet of oxygen is produced inside the chimney, burning in an atmosphere of cal-gas. A jet of air may also be employed, under favourable conditions as to relative position of jet and chimney, strength of gas and oxygen streams, &c., a



singing flame is produced like the ordinary hydrogen flame in a glass tube (chemical harmonica).

C. R. A. W.

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### Inorganic Chemistry.

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**Solidifying Point of Bromine.** By H. BAUMHAUER (Deut. Chem. Ges. Ber. iv, 927).

THE solidifying point of bromine is variously given as  $-7^{\circ}$ ,  $-7^{\circ}3$ ,  $-18^{\circ}$ ,  $-22^{\circ}$ ,  $-25^{\circ}$ . The author finds  $-24^{\circ}5$  as the result of his redetermination of this point. Solidified bromine is a red-brown crystalline mass. The presence of water raises the solidifying point, owing to the formation of hydrate, which probably accounts for the high number,  $-7^{\circ}$ , above referred to.

H. E. A.

**Preparation of Ozone in a Concentrated State.** By A. HOUZEAU (Compt. rend., lxxiv, 256).

IN an ordinary straight gas-delivery tube is placed a wire of copper, lead, or better, of platinum, 4 to 6 decimeters long, with one of its extremities passing through the side of the upper portion of the tube. On the exterior of the tube is coiled a similar wire over the path of the preceding. When the two are placed in communication with a Ruhmkorff's coil giving a 2 or 3 centimeter spark, a slow stream of oxygen passing through the tube will be strongly charged with ozone. By this apparatus, called by the author an "ozonizer," he has prepared oxygen containing 60 to 120 (once 188) milligrams of ozone per litre. Electrolysis of water furnished only 3 to 5 milligrams, barium peroxide and sulphuric acid 10 milligrams, per litre.

C. G. S.

**Note on the Action of Sulphur on Vapour of Water; on the Synthesis of Sulphuric Acid; and on the preparation of Pure Zinc by Electrolysis.** By V. MEYER (Compt. rend., lxxiv, 195).

*I. Action of Sulphur on Water-vapour.*—The fact that sulphur at a red heat decomposes water was discovered by Mulder in 1858, and confirmed by Gripon and by Corenwinder. The author passes steam over boiling sulphur in a tube, and condenses the slightly acid product.

The liquid cannot be concentrated without decomposition. In examining the nature of the product, the author observes that the reactions given in books for the thionic acids are not sufficiently characteristic. He therefore, by solution of iodine, which is decolorised by sulphurous and thiosulphuric, but not by the other thionic acids, proved the product to be one of the two former. By Böttger's reaction with alkaline permanganate, which is turned green by sulphites but decolorised by

thiosulphates, in dilute solutions (1 in 3,000), he proved it to be hyposulphurous.

The author has kept the liquid more than a year, and still obtains the same reactions. At 30° C. it splits up into sulphurous acid and sulphur. Mercuric chloride gives with it a yellow precipitate; mercurous nitrate a black precipitate; cupric sulphate on heating a black precipitate of sulphide; silver nitrate a white precipitate, soon becoming brown. Schützenberger's hydrosulphurous (hyposulphurous) acid, which cannot exist long in the free state, reduces silver nitrate.

II. *Synthesis of Sulphydric Acid*.—This acid decomposes at 400°. However, as several chemists have asserted that its direct synthesis is possible, the author purified hydrogen by passing it through solutions of lead acetate, lead oxide in potash, silver nitrate, and mercuric chloride, then through fragments of porcelain at a bright red heat, and finally into calcium chloride and phosphoric anhydride. When this gas was passed over boiling sulphur, traces of sulphydric acid were formed. The author tried to prepare pure hydrogen by electrolysis, but could not obtain a sufficiently rapid current.

III. *Preparation of pure Zinc by Electrolysis*.—When an ammoniacal solution of zinc sulphate is decomposed by the galvanic current, the positive electrode consisting of a plate of zinc, and the negative of a copper wire shaped like a T, crystals of zinc are deposited on the latter. A potash-solution of zinc sulphate was tried without success.

C. G. S.

### Action of Heat on the Oxychlorides of Silicon. By L. TROOST and P. HAUTEFEUILLE (Compt. rend., lxxiv, 111).

WHEN oxychloride of silicon is distilled at a temperature exceeding 440°, the evidence of incipient decomposition becomes apparent, from the production of dense white fumes in the vessel in which the distillation is carried on.

The authors have studied this reaction more closely, with the following results:—The vapour of the oxychloride,  $\text{Si}_4\text{O}_2\text{Cl}_6$ , was passed through a glass tube filled with fragments of porcelain, and heated to redness. During the operation, neither oxygen nor chlorine was liberated, neither was there any appreciable loss of weight; but on submitting the product to fractional distillation, it was found that, while the boiling point of the oxychloride was nearly constant at 136°, the new liquid began to boil at 59°; two-thirds of the liquid distilled at and below the boiling point of the oxychloride, and the remaining third at temperatures varying from 150° upwards.

About one-half of the distillate consisted of tetrachloride of silicon, regenerated by the action of heat upon the oxychloride; one-fourth was oxychloride which had escaped decomposition, and the remaining third or fourth part, the boiling point of which was above 150°, constituted a complete series of oxychlorides,  $\text{Si}_4\text{O}_3\text{Cl}_5$ ,  $\text{Si}_8\text{O}_8\text{Cl}_8$ ,  $\text{Si}_{16}\text{O}_{20}\text{Cl}_{12}$ ,  $\text{Si}_{4n}\text{O}_{6n}\text{Cl}_{2n}$ , produced by molecular condensation, and in which the

ratio of oxygen to silicon was greater than in the oxychloride from which they were produced.

The proportions in which these oxychlorides occurred in the original distillate, varied according to the temperature and rapidity with which the operation was conducted; it was noticed, as a rule, that the condensation was greatest, when the temperature was high and its action considerably prolonged.

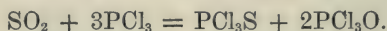
J. W.

**On the Action of Phosphorous Chloride upon Anhydrides and Chlorides.** By A. MICHAELIS (*Jenaische Zeitschrift*, vii, 110—117).

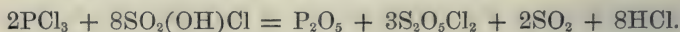
WHEN the compound upon which phosphorous chloride acts, contains any substances having a great affinity for chlorine, a large amount of phosphoric acid with but little phosphorus oxychloride, is produced.

The author gives the reactions which he observed to take place when phosphorous chloride was allowed to act upon many different anhydrides and chlorides. The following equations represent the reactions which, from these experiments, seem to take place in each case:—

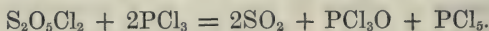
1. With sulphurous anhydride, the vapours being passed through a heated tube—



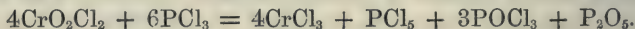
2. With sulphuric chlorhydrate (sulphuryl-hydroxyl chloride), a reaction takes place in the cold, expressed thus—



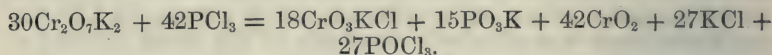
3. With hyposulphuric chloride (pyrosulphuryl chloride)—



4. With chromium oxychloride the reaction is exceedingly energetic, accompanied by a hissing noise and evolution of light. It may be thus formulated—



5. Heated to  $166^\circ$  in a sealed tube with potassium bichromate, phosphorous chloride acts in a way which the author represents thus—



6. With antimonious hydrate, as well as with metallic antimony, phosphorous chloride gives free phosphorus, phosphoric anhydride, and antimonious chloride, while with antimonie oxide, after heating to  $160^\circ$  in a sealed tube, phosphoric anhydride and antimonious chloride are formed. With bismuthous oxide the reaction is somewhat different, and may be formulated thus—





7. When the chloride is heated over a lamp with lead monoxide (PbO), metallic lead, lead chloride, and lead phosphate are produced. If lead dioxide (PbO<sub>2</sub>) be employed, then no metallic lead is formed, but lead chloride, lead phosphate, and phosphorus oxychloride.

8. Stannic oxide and phosphorous chloride heated to 160° give stannous and stannic chlorides, together with phosphoric anhydride. With cupric oxide, cuprous and cupric chlorides, tricupric phosphate, and phosphorus oxychloride are formed, according to the equation—



The reaction with mercuric oxide is completely analogous to that with the copper salt.

Molybdic trioxide acts on phosphorous chloride when heated to 160°, giving rise to phosphoric anhydride and molybdic oxychloride (MoO<sub>3</sub>Cl<sub>2</sub>).

Upon the oxides of iron, manganese and tungsten, phosphorous chloride has no action.

M. M. P. M.

### Decomposition of Phosphorous Chloride by Water. By

A. GEUTHER (Jenaische Zeitschrift, vii, 122—126).

THE author refers to the statement of Kraut (*Ann. Chem. Pharm.* clviii, p. 133), to the effect that, on dropping pure phosphorous chloride into boiling water, as each drop touches the water, a bright flame is seen, and there is a deposit of amorphous phosphorus.

With water at 80°, the author found only a very slight deposition of phosphorus; with water which had been boiling for a moment before the experiment, he noticed an appearance near the mouth of the test tube which contained the water, much resembling phosphorescence, but no phosphorus was separated. By varying the conditions of his experiments, he has been led to conclude that it is only in presence of an excess of air that the phosphorescent phenomena are exhibited by the phosphorous chloride when dropped into water.

He supposes that part of the phosphorous chloride is rendered gaseous; this is decomposed, giving hydrochloric acid, and phosphorous acid, which, by the excess of oxygen present, is oxidised to phosphoric acid; a small part of the phosphorous acid formed, he supposes, may be reduced to phosphuretted hydrogen, and this again decomposed, giving water and free phosphorus, and hence the small quantity of separated phosphorus.

Distilled with a solution of phosphoric acid, phosphorous chloride gives hydrochloric acid, free phosphorus, and phosphorous oxychloride.

M. M. P. M.

### Composition of Antimonious Hydrate. By A. GEUTHER

(Jenaische Zeitschrift, vii, 121).

By precipitating a solution of potassium antimonate with nitric acid, washing the precipitate with cold water, and allowing it to dry at

the ordinary temperature during a whole summer season—the author has obtained a substance which, on analysis, gives numbers corresponding to the formula  $\text{H}_3\text{SbO}_4$ ; this he regards as standing midway between the hydrate obtained by Berzelius,  $\text{HSbO}_3$ , and that obtained by Fremy,  $\text{H}_5\text{SbO}_5$ . The new substance, heated to  $175^\circ$ , is transformed into the hydrate obtained by Berzelius.

M. M. P. M.

### Decomposition of the Soluble Metallic Sulphides by Water.

By H. KOLBE (J. pr. Chem. [2] iv, 412—417).

J. THOMSEN, from the results of his thermochemical researches on sulphuretted hydrogen (*Pogg. Ann.*, cxl, 526), considers the latter to be a monobasic acid  $\text{H.SH}$ , and concludes that the normal sulphides when dissolved in water, are to be regarded as mixtures of hydrates and sulphydrates of the general formula  $\text{R.SH}$ . This view is supported by the fact that the action of water on normal barium sulphide decomposes it into barium sulphydrate and barium hydrate. Such a decomposition of the aqueous solution, however, does not happen in the case of sodium sulphide. A solution of the crystalline sodium sulphide,  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , when boiled with potassium ethyl sulphate, should yield mercaptan without any admixture of ethyl sulphide, if the action of water had effected complete decomposition into sodium hydrate and sodium sulphydrate. The author finds, however, that ethyl sulphide is the principal product of the reaction, being accompanied by more or less mercaptan, according to the strength of the solutions employed; the weaker the solution the larger being the proportion of mercaptan. From the results of his experiments he infers that the metallic sulphides are only partly decomposed into hydrates and sulphydrates by solution, the extent of the decomposition depending on the proportion of water present.

C. E. G.

### The Spontaneous Decomposition of various Acid Sulphites.

By C. SAINT-PIERRE (Compt. rend., lxxiv, 52).

THE author having noticed that a solution of acid potassium sulphite, when heated in a sealed tube, was decomposed, with production of sulphuric acid and free sulphur, publishes further experiments on this subject. Liquid sulphurous anhydride and concentrated solutions of sulphurous acid were found to bear, under pressure, the temperature of a water-bath for an unlimited time without decomposition. A solution of acid lead sulphite, treated in a similar manner, quickly produced a precipitate of lead sulphate; and on opening the tube, the solution was found to contain free sulphuric acid and an acid of the thionic series. No lead remained in solution.

By heating a solution of acid barium sulphite in a sealed tube for twelve hours, the barium was completely precipitated as sulphate. The solution, as in the previous instance, contained free sulphuric acid and a small quantity of an acid containing a larger proportion of sulphur; the latter being recognised by the black precipitate which it afforded with the salts of mercury and silver. The barium sulphate

was exhausted with carbon disulphide, but no free sulphur had been deposited.

J. W.

### Amount of Combined Water in certain Double Sulphates.

By H. RHEINECK (Dingl. Polyt. J., ccii, 268—271).

*Ammonio-ferrous Sulphate*.—The author finds this salt to have the composition  $(\text{NH}_4)_2\text{Fe}''(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$ . The direct determination of the water being impossible on account of oxidation and loss of ammonia during the drying process, a portion of the salt was dried at  $110^\circ \text{C}$ . for six hours, and finally at  $120^\circ$ , till no further loss of weight occurred. In the residue dissolved in water, the unchanged ferrous oxide was estimated with permanganate solution, and then the residual ammonia, by distillation with lime into titrated acid solution.

The molecular weight of the salt was also determined by the estimation of the ferric oxide obtained in the usual way, and by gently igniting a portion of the salt, moistening with ammonia solution, and again igniting, until the weight remained constant.

*Potassio-ferrous Sulphate*,  $\text{K}_2\text{Fe}''(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$ .—In this salt the water was determined by the indirect method above referred to. Only four molecules could be expelled at a temperature of  $110^\circ$ .

*Ammonio-magnesium Sulphate*,  $(\text{NH}_4)_2\text{Mg}''(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ . *Ammonio-cupric Sulphate*,  $(\text{NH}_4)_2\text{Cu}''(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .

The author concludes that the general formula,  $\text{R}_2\text{M}''(\text{SO}_4)_2 + 6\text{H}_2\text{O}$ , usually adopted in text-books, does not hold good, but that two groups are formed from the root formula,  $\text{M}''\text{SO}_4 + 7\text{H}_2\text{O}$ ; 1stly, one in which  $\text{H}_2\text{O}$  may be said to be replaced by  $\text{R}_2\text{SO}_4$ ; and 2ndly, one in which  $(\text{H}_2\text{O})_2$  may be said to be replaced by  $\text{R}_2\text{SO}_4$ .

W. S.

### Amount of Combined Water in Ferrous Sulphate precipitated by Alcohol. By G. H. BARCKHAUSEN (Arch. Pharm. [2], cxlviii, 197—199).

IN most Handbooks of Chemistry the composition of ferrous sulphate precipitated by alcohol, is said to be the same as that of ferrous sulphate crystallised from water. The author dissolved 50 grams of the salt in 50 grams of water and precipitated it with 50 grams of alcohol. The crystalline precipitate when exposed in dry air at  $18^\circ \text{C}$ . had not the composition of the crystallised sulphate. The amount of iron contained in it more nearly corresponded to that in a salt having 6aq. instead of 7aq., and by keeping the compound only for a few hours the proportion of the ferrous oxide rose considerably, showing that the salt continued to lose water at ordinary temperatures.

A. P.

### On the Diffusion of Mercurial Vapours. By MERGET (Compt. rend., lxxiii, 1956).

THE author appears to have conclusively proved the invalidity of Faraday's conclusions respecting the evaporation and diffusion of



mercury. He finds that ammoniacal nitrate of silver is a far more delicate test of the existence of mercury vapour than gold leaf, and by means of this reagent he has shown that the vaporisation of mercury is a continuous phenomenon, occurring even when the metal is solidified. The action of mercury vapour on salts of the noble metals evidently admits of a variety of important practical applications: among others the author describes a process of obtaining permanent photographs.

T. E. T.

### Mineralogical Chemistry.

**On a Complex Alum obtained from the Hot Mineral Water of the Solfatara of Puzzuoli.** By S. DE LUCA (*Compt. rend.*, lxxiv, 123).

THE examination of the water of this mineral spring, the results of which were communicated in the *Académie des Sciences* in February, 1870, showed that it contains, not only sulphuric acid, but also several bases, which, on combining with the acid, ought to produce a complex alum. A quantity of the water was therefore concentrated to a tenth of its original bulk, and, after being carefully filtered, was left to crystallise by spontaneous evaporation. The slow evaporation went on for about a year, and at the end of that time fine crystals, having the form of ordinary alum, were obtained.

These crystals, when moderately heated, gave off a large quantity of water, and, on the application of a higher temperature, sulphurous acid fumes and a sublimate of solid matter. When they were heated with caustic potash, ammonia came off freely. Their density, taken in alcohol at 17° C., was 1.774 compared with water at the same temperature.

The following is the result of an analysis of the crystals:—

Sulphuric acid .....	36.74
Alumina .....	6.70
Ammonium oxide (NH <sub>4</sub> ) <sub>2</sub> O.....	10.82
Ferrous oxide .....	0.97
Ferric oxide .....	1.10
Lime .....	0.65
Magnesia .....	0.30
Potash .....	0.17
Water .....	40.98
Soda, manganese oxide, and loss ....	1.57

Total..... 100.00

The mother-liquor was extremely acid, and contained, besides the materials just mentioned, traces of chlorine, a small quantity of nitrogenous organic matter, and a large quantity of silica.

J. T. B.

**Siderite, pseudomorphously crystallised in the forms of Calc-spar and Bitter Spar.** By H. STRÜVER (Note mineralogische. Torino, 1871, p. 22—25; Jahrbuch f. Mineralogie, 1871, 883).

SUBSTITUTION-PSEUDOMORPHS of siderite after calc-spar are somewhat rare. The Turin collection possesses two interesting specimens from Brozzo, consisting of pyrite crystals of the combination  $\frac{\infty O_2}{2} \cdot \frac{4O_2}{2}$ .

$O \cdot \infty O\infty$ , on which are implanted crystals having the form of calc-spar, bitter spar, and mesitine. The scalenohedrons, however, consist of a granular aggregate of siderite containing 94·30 p. c.  $FeCO_3$ , 3·04  $MgCO_3$ , and 2·68  $CaO_3$ , the lime having been almost wholly replaced by ferrous oxide. Side by side with the scalenohedrons are implanted crystals of bitter spar, more or less altered to siderite. Nearly all of them, however, still contain nuclei of magnesio-calcic carbonate, which fills up the little cavities left by the siderite in the substitution process, and follows the directions of cleavage, forming a kind of network. The lenticular crystals of mesitine have remained unaltered, being merely covered with a thin crust of siderite.

H. W.

**Crystallographic Studies:—Scheelite.** By MAX BAUER (Jahrbuch f. Mineralogie, 1871, 879). **Selenite.** By F. SCHRAUF (*ibid.* 881).

**Composition of the Labradorite Rocks of Waterville, New Hampshire.** By E. S. DANA (Am. J. of Sci. [3] iii, 48).

Two specimens of feldspathic rock, obtained by Prof. Hitchcock from the locality of Waterville, and supposed to be labradorite, were submitted to analysis with the following results. The first was a dark-coloured rock, consisting principally of triclinic feldspar, with small yellowish grains of chrysolite. The feldspar possessed a dark smoky colour, which the microscope showed to be due to the presence of very minute grains of magnetic iron ore, from about  $\frac{1}{56}$ th to  $\frac{1}{200}$ th of an inch in diameter. It gave the following percentage composition:—

$SiO_2$ .	$Al_2O_3(TiO_2)$ .	$Fe_2O_3$ .	$CaO$ .	$Na_2O$ .	$K_2O$ .
51·03	26·20	4·96	14·16	3·44	0·58 = 100·37

The analyses of the mineral supposed to be chrysolite afforded—

$SiO_2$ .	$Al_2O_3$ .	$Fe_2O_3$ .	$MnO$ .	$MgO$ .	$CaO$ .
38·85	trace	28·07	1·24	30·62	1·43 = 100·19

The large percentage of iron present in the chrysolite is remarkable. It is an essential constituent of the mineral, and not owing to the presence of impurities. The second specimen of rock was different in appearance from the first. Its principal constituents were feldspar and hornblende, associated with a little magnetic iron ore, mica, and a green mineral, probably epidote. No chrysolite was present.

Two analyses afforded—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MgO.	CaO.	Na <sub>2</sub> O <sub>3</sub> .	K <sub>2</sub> O.
52·25	25·71	1·08	0·99	13·22	3·68	2·18 = 99·11

J. W.

**The relative proportion of Iron and Sulphur in the Pyrites contained in certain Specimens of Iowa Coal.** By RUSH EMERY (Am. J. of Sci. [3] iii, 34).

THE following examination was undertaken with the view of ascertaining whether the amount of sulphur contained in Iowa coal, was greater than would be necessary to form with the iron the combination FeS<sub>2</sub>.

The coal, in the first instance, was treated with very dilute hydrochloric acid, so as to remove everything which was soluble in that menstruum. The residue was then oxidised with hydrochloric acid and potassium chlorate, and the percentage of iron and sulphur calculated in the usual manner. The absence of calcium sulphate in the residue before oxidation was carefully ensured.

Ten samples were examined. In four samples the relative proportions of iron and sulphur corresponded very closely with that existing in FeS<sub>2</sub>, viz., 53·3 per cent. In four samples there was a decided excess of sulphur, the percentage rising in two instances to 63·0 per cent., while in two samples there was a marked deficiency of sulphur 45·0 and 50·0 per cent. only being found.

The results of the analyses of the coals of Ohio, by Prof. Wormley, showed that in every instance the amount of sulphur present was too large for combination with the iron as disulphide.

J. W.

### Origin of Coal (Chem. Centr., 1871, 815).

ACCORDING to Wurtz, the formation of coal is intimately connected with the action of iron dissolved in the waters of the carboniferous period, being in fact the normal product of a special eremacausis of organic substances in waters holding sulphate of iron and free carbonic acid in solution.

C. H. G.

### Organic Chemistry.

**An Important Improvement in the Method of Fractional Distillation.** By EDUARD LINNEMANN (Ann. Chem. Pharm., clx, 195—242).

THE improvement consists in the use of thimble-shaped pieces of platinum gauze, inserted into the tube connecting the distilling flask with the condenser. The number of the gauze cups depends upon the volatility of the liquids which have to be fractionated; for liquids boiling



below  $150^{\circ}$  the author employs a tube containing 5 cups; for liquids boiling up to  $180^{\circ}$  6 cups; for liquids possessing still higher boiling points 5 cups are found to be sufficient. Full details of the method employed in making the gauze cups, together with the dimensions found to be most useful, are given in the paper, which is, moreover, illustrated by a wood cut. The author claims two advantages for his improvement. In the first place it allows of a more complete purification of liquids by fractional distillation than has hitherto been found practicable, and, in the second place, it allows the determination of the boiling point of a liquid to be made with greater accuracy, all superheating of the vapour being avoided.

The author gives a variety of examples of fractional distillation made by his method, together with a number of determinations of the boiling points (reduced and corrected) of some important derivatives of ethyl, propyl, and butyl alcohols.

Ethyl iodide . . . .	$72^{\circ}38\text{ C.}$	Sp. gr. at $14^{\circ}5$	1.9444
Ethyl benzoate ..	$211^{\circ}16$	" $16^{\circ}$	1.0502
Ethyl acetate ...	$77^{\circ}00$	" $15^{\circ}$	0.9068
Ethyl propionate {	$98^{\circ}80$	" $17^{\circ}$	0.8945
	$98^{\circ}84$	" $16^{\circ}$	0.8964
Ethyl alcohol....	$78^{\circ}53$	" $17^{\circ}$	0.8090
Ethyl bromide ..	$38^{\circ}78$	" $13^{\circ}5$	1.4685
Ethyl chloride ..	$12^{\circ}18$	" $8^{\circ}$	0.9176
Acetic acid.....	$118^{\circ}10$ (m. p. $16^{\circ}5$ )	" $20^{\circ}$	1.0026
Propionic acid .. {	$140^{\circ}71$	" $19^{\circ}$	0.9961
	$140^{\circ}67$		

He has also described a few propionates.

The *calcium salt* requires 1.87 parts of water for solution at  $17^{\circ}$ . The barium salt is anhydrous, and requires 1.67 parts of water for solution at  $17^{\circ}$ . The apparent crystalline form of the *silver salt* varies with the temperature of crystallisation; at one time it separates out in plates, at another in needles. On this account silver propionate can scarcely be recognised by its form; when perfectly pure, and in large quantity, it generally crystallises in broad shining needles. 1 part of the salt requires for solution 119 parts of water at  $18^{\circ}$ .

The neutral *lead salt* is easily soluble, but does not crystallise, the basic salt crystallises occasionally in the form of needles. It is soluble in from 8 to 10 parts of water at  $14^{\circ}\text{ C.}$  A cold saturated solution, heated to the boiling-point, and shaken, deposits nearly all the salt, and the liquid appears to become almost solid. The salt filtered from the hot solution, and dried over sulphuric acid, has the formula  $3\text{Pb}(\text{C}_3\text{H}_5\text{O}_2)_2 \cdot 4\text{PbO}$ . By means of this salt propionic acid may be separated from formic and acetic acids. If a mixture of the three acids in water is evaporated to dryness with an excess of lead oxide, cold water will extract only basic lead propionate, and on heating the clear cold solution, the lead salt will be precipitated, the slight traces of accompanying lead acetate and formate remaining in solution.

Since basic lead acrylate is also almost insoluble in cold water, the formation of the lead salt offers a ready method of detecting and

separating even small quantities of propionic acid in presence of acrylic acid. The author shows by analysis that the propionic acid so separated is pure. This acid, according to the author, is never produced by the fermentation of lactic acid. In his investigations on butyric acid he found that but little of the acid which comes into commerce under that name can be regarded as even approximately pure.

Normal butyric acid boils at  $162.30^{\circ}$ , has a sp. gr. of 0.9580 at  $14^{\circ}$ , freezes at  $-19^{\circ}$  to a crystalline mass; begins partially to melt at  $-2^{\circ}$ , and is completely liquid at  $+2^{\circ}$ . *Ethyl butyrate* prepared by Pelouze's method boils at  $121.09^{\circ}$ ; sp. gr. at  $17^{\circ}$  0.8990. *Silver butyrate* requires for solution 202 parts of water at  $14^{\circ}$ , and 72 of boiling water. The *calcium salt* crystallises in broad transparent brilliant needles; 1 part dissolves in 3.6 of water at  $14^{\circ}$ . A cold saturated solution solidifies almost completely on heating. The *barium salt* closely resembles the preceding compound; it is soluble in 2.43 parts of water.

The author shows the value of his method in the separation of propyl and butyl alcohols from the products of the alcoholic fermentation of corn and molasses. He cannot recommend ordinary fusel oil as a source of propyl or butyl alcohol, since this liquid in general contains but small quantities of these alcohols. He prefers the distillate obtained in the spirit-refining process at that particular point when it acquires an altered specific gravity, a scarcely perceptible fusel odour, and a slight turbidity.

The product obtained at this point contains a considerable amount of water, smells faintly of fusel oil, and is rendered turbid on being further mixed with water. This alcoholic liquid, after drying over potassium carbonate, is distilled on the water-bath, all the ethyl alcohol being obtained in the distillate which comes over up to  $83^{\circ}$ . After treatment with powdered potash, boiling with inverted condenser on the water-bath, addition of an equal volume of water, drawing off the layer of alcohol, and drying over potassium carbonate, the product is fractionated, whereby pure propyl alcohol, considerable quantities of isobutyl alcohol, and amyl alcohol, are obtained.

From 8 litres of the above-mentioned product of the spirit refinery were obtained—

5 litres ethyl alcohol fractionated	77° to 85°.
450 grams propyl and butyl alcohol fractionated	85° to 115°.
700 grams amyl alcohol in the residue.	

From these 8 litres were obtained about 60 grams of propyl alcohol in the form of pure propyl iodide.

The author considers that the propyl alcohol obtained by simple distillation from fermentation-products by Pierre, Puchot, and Chancel, was not pure, but that by using his improvement in fractional distillation pure propyl and butyl alcohol may be easily obtained.

The pure isobutyl alcohol which the author obtained was a perfectly colourless, optically inactive, liquid, having a very slight odour of fusel oil. 1 part of this alcohol dissolved 15 parts of water at  $15^{\circ}$ . The sp. gr. at  $18^{\circ}$  is 0.8003. The boiling-point is given as  $108.39^{\circ}$ .

From the various distillates mentioned above the author has prepared ethyl, propyl, and butyl iodides.

The boiling point of normal propyl iodide he gives as  $102.95^{\circ}$ , and its sp. gr. as 1.7472 at  $16^{\circ}$ .

Isobutyl iodide has a boiling point, as determined by the author, of  $120.63^{\circ}$ .

T. E. T.

**On the Reducing Action of the Hydrogen absorbed by Palladium.** By H. KOLBE (preliminary notice) (*J. pr. Chem.* [2] iv, 418—419).

THE author hoped to effect the direct conversion of the acids into the corresponding alcohols, or aldehydes, by means of this reducing agent, but from want of time he has placed the research in the hands of his pupil, Herr Saytzeff. The latter, by passing a mixture of chlorobenzoyl vapour and hydrogen over heated palladium-black, obtained hydrochloric acid, and an oil which is apparently benzoic aldehyde, mixed with benzyl alcohol. It forms a crystalline compound with acid sodium sulphite. He has also, in a similar manner, succeeded in reducing nitrobenzene to aniline, and is about to try its action on benzoic anhydride, acetic acid, &c., with the object of converting them into benzylic alcohol and ethylic alcohol.

C. E. G.

**On Acetylene and Allylene.** By E. CARSTANJEN (*J. pr. Chem.* [2] iv, 419—426).

FROM the readiness with which acetylene exchanges its hydrogen for metals, the author infers that of the two possible isomeric modifications

I.  $\begin{array}{c} \text{CH}=\text{CH} \\ | \quad | \\ \text{CH}=\text{CH} \end{array}$  II.  $\begin{array}{c} \text{C}\equiv\text{C} \\ | \quad | \\ \text{CH}_2-\text{CH}_2 \end{array}$  the first represents acetylene, and considers that

the precipitate produced by it in an ammoniacal silver solution has the

formula  $\begin{pmatrix} \text{CAg} \\ | \\ \text{CAg} \end{pmatrix}_2 + \text{H}_2\text{O}$ , and not  $\begin{array}{c} \text{C}_2\text{HAg} \\ \text{C}_2\text{HAg} \end{array} + \text{Ag}_2\text{O}$  as usually represented.

Berthelot's argentacetyl chloride,  $(\text{C}_2\text{Ag}_2\text{H})\text{Cl}$ , would then

be  $\begin{array}{c} \text{CAg} \\ | \\ \text{CAg} \end{array} + \text{HCl}$ . With regard to the other modification of acetylene,

$\begin{array}{c} \text{C}\equiv\text{C} \\ | \quad | \\ \text{CH}_2-\text{CH}_2 \end{array}$ , if it should exist, he believes that it would probably be in-

capable of exchanging its hydrogen for a metal.

Six isomeric modifications of allylene, the second member of the

series  $\text{C}_n\text{H}_{2n-2}$ , are possible; of these the author considers  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{C}=\text{CH} \\ | \\ \text{CH}=\text{CH} \end{array}$

to be that of ordinary allylene, especially as Borsche and Fittig (*Ann. Ch. Pharm.* cxxxiii, 120) have obtained it directly from dichloroacetone



chloride, whose formula is  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CCl}_2 \\ | \\ \text{CHCl}_2 \end{array}$ . An isoallylene of the formula

$\begin{array}{c} \text{CH}_2- \\ | \\ \text{C}= \\ | \\ \text{CH}_2- \end{array}$  incapable of exchanging its hydrogen for metals, would probably

be obtained from isodichloracetone chloride,  $\begin{array}{c} \text{CH}_2\text{Cl} \\ | \\ \text{CCl}_2 \\ | \\ \text{CH}_2\text{Cl} \end{array}$ , prepared by the

action of phosphoric chloride on isochloracetone,  $\begin{array}{c} \text{CH}_2\text{Cl} \\ | \\ \text{CO} \\ | \\ \text{CH}_2\text{Cl} \end{array}$ . This reaction

the author is at present investigating. It is possible that the gas obtained by Pfeffer and Fittig (*Ann. Ch. Pharm.* cxxxv, 357), by the action of sodium on tetrachloroglycide, and which was not absorbed by an ammoniacal copper solution, was an isoallylene, and not propylene, as they supposed.

C. E. G.

### On Two New Chlorobromides of Carbon. By E. PATERNÒ (*Gazzetta Chimica Italiana*, i, 593—595).

*Action of Bromine on Chloroform.*—By heating chloroform with bromine to 200° for six or eight hours, washing the product, and submitting it to fractional distillation, the author obtained a liquid boiling at 104.3° at 757.9 millim., and having the composition  $\text{CCl}_3\text{Br}$ . It is mobile and colourless, but becomes coloured by exposure to light; it has a pleasant ethereal odour, and dissolves in alcohol and ether. A small quantity of a liquid boiling at a higher temperature, probably  $\text{CCl}_2\text{Br}_2$ , is also obtained in this reaction.

*Action of Bromine on Pentachlorethane.*—On heating the latter with bromine to 200°, it is transformed into a solid crystalline substance, which may be purified by washing with dilute potash, and crystallisation from alcohol or ether, in which it is very soluble. It has a characteristic camphoric odour, similar to that of carbon trichloride, which it closely resembles in appearance. When heated it decomposes, with liberation of bromine, but without melting or volatilising. It has the formula  $\text{C}_2\text{Cl}_4\text{Br}_2$ , or  $\begin{array}{c} \text{CCl}_3 \\ | \\ \text{CClBr}_2 \end{array}$ , that of the isomeric compound obtained by Malaguti by the direct union of bromine and carbon protochloride,  $\text{C}_2\text{Cl}_4$ , being  $\begin{array}{c} \text{CCl}_2\text{Br} \\ | \\ \text{CCl}_2\text{Br} \end{array}$ .

C. E. G.

**On Ethylidene Bromide.** By E. PATERNO and G. PISATI (*Gazzetta Chimica Italiana*, i, 596—598).

As chlorinated ethyl chloride is known to be identical with ethylidene chloride, whilst brominated ethyl bromide differs entirely from the so-called ethylidene bromide, which Wurtz and Frapolli (*Ann. Ch. Phys.*, lvi, 144) obtained by the action of phosphorus perbromide on aldehyde, there has existed considerable doubt whether the latter compound is really ethylidene bromide. The authors' results, obtained by the action of phosphorus pentachloride on dichloraldehyde, induce them to believe that it is probably an oxybromide of ethylidene analogous to the oxychloride described by Lieben. On adding aldehyde to phosphorus bromochloride,  $\text{PCl}_3\text{Br}_2$ , treating the product with water, and distilling in a current of steam, an oily product is obtained, which by rectification gives a liquid of the formula  $\text{C}_2\text{H}_4\text{Br}_2$ , boiling at  $110^\circ$ — $112^\circ$ . Its mode of formation shows it to be the true ethylidene bromide, and from its boiling point it would seem to be identical with the brominated ethyl bromide obtained by Hofmann and Caventon by the action of bromine on ethyl bromide, and by Reboul (*Compt. rend.* lxx, 399), by that of hydrogen bromide on brominated ethylene. The less volatile portion of the product appears to contain more highly brominated derivatives of ethylidene, as an analysis of that body at about  $180^\circ$  corresponded very nearly with the formula  $\text{C}_2\text{H}_3\text{Br}_3$ . C. E. G.

**Contributions to the History of Nitrosodiethylin.** By A. GEUTHER (*Jenaische Zeitschrift*, vii, 118—121).

WITH alkaline bases, as potassium or sodium hydroxides, whether these be in a watery or an alcoholic solution, when heated in sealed tubes to  $155^\circ$  for eight hours, nitrosodiethylin reacts somewhat energetically.

After the reaction there is obtained, by distillation from the water-bath, a liquid which, on addition of hydrochloric acid, and subsequent treatment with platinum chloride, gives ammonium platinochloride, and in the filtrate therefrom ethylammonium platino-chloride. Thus ethylamine and ammonia are simultaneously produced.

Sodium amalgam, in presence of water, exerts a vigorous action on nitrosodiethylin, and from the analysis of the platinum salt obtained from the liquid distilled off after this action had ceased, it is seen that diethylamine is produced, together with nitrous oxide.

Dry chlorine gas, in presence of carbon dioxide, transforms the liquid nitrosodiethylin into a mass of crystals, which, after washing with ether, were proved to be diethylammonium chloride, chloride of nitrosyl being formed at the same time.

These three reactions are formulated by the author thus—

1.  $4\{(\text{C}_2\text{H}_5)_2\text{NO.N}\} + 8\text{KHO} = *4\{(\text{C}_2\text{H}_5)_2\text{HN}\} + 2\text{NH}_3 + 2\text{C}_2\text{H}_4 + 2\text{N} + 4\text{K}_2\text{CO}_3 + 3\text{H}_2\text{O}.$
2.  $2\{(\text{C}_2\text{H}_5)_2\text{NO.N}\} + 4\text{H} = 2(\text{C}_2\text{H}_5)_2\text{HN} + \text{N}_2\text{O} + \text{H}_2\text{O}.$
3.  $(\text{C}_2\text{H}_5)_2\text{NO.N} + 2\text{HCl} = (\text{C}_2\text{H}_5)_2\text{H}_2\text{NCl} + \text{NOCl}.$

M. M. P. M.

\* The quantities of oxygen on the two sides of this equation do not agree.—Ed.

**Reduction of Formic Acid to Formaldehyde and Methyl Alcohol.** By E. LINNEMANN and V. VON ZOTTA (*Ann. Chem. Pharm.*, clxi, 15—17).

THE same process as that given by Lieben and Rossi (*ibid.*, clviii, 107; *Chem. Soc. J.*, 1871, p. 343).

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**Synthesis of Normal Propyl Alcohol.** By E. LINNEMANN (*Ann. Chem. Pharm.*, clxi, 18—25).

IN a former communication (*Ann. Chem. Pharm.*, cxlviii, 257) Linnemann has shown that by the action of sodium amalgam upon propionic anhydride, normal propyl alcohol is formed. 76 grams of the crude anhydride yield 3.2 grams of crude alcohol, besides sodium propionate, from which 76 grams of propionic acid could be isolated. To obtain a pure product, the alcohol was converted into the iodide, and this into the benzoate, from which by saponification, pure propyl alcohol was obtained.

Another method to reduce propionic acid to the alcohol is to distil a mixture of pure and dry calcium propionate and formate, and act on the aldehyde with sodium amalgam. But by employing this method, Linnemann and Siersch did not at first succeed in obtaining the aldehyde, because they destroyed this very changeable body by trying to isolate the pure aldehyde from its compound with sodium bisulphite. Since that time, however, Rossi obtained good results by using the crude aldehyde, and Linnemann has now also succeeded, in reducing propionic acid to propyl alcohol by this method. 100 grams of propionic acid yielded 16 grams of aldehyde boiling between 41°—55°, the chief portion distilling at 48.1°—50.1°. By subjecting this portion to a systematic fractional distillation, the corrected boiling point was found to be 48.77°.

Its specific gravity is 0.8074 at 21°; it is soluble in water, one volume dissolving in five volumes of water at 20°. With sodium bisulphite it forms a crystalline compound, from which, by means of sodium carbonate, the aldehyde can again be separated; but by acting on a concentrated solution of the bisulphite compound with a solution of caustic potash, the aldehyde is converted into a liquid boiling between 120°—125°.

By acting on the aqueous solution of the aldehyde with sodium amalgam in the cold, only one-sixth of it is converted into alcohol, lower and higher boiling products being formed at the same time.

In order to obtain from it other pure propyl-compounds, it was converted into the iodide, which was purified by fractional distillation. The pure iodide boiled at 102.11° (corr.). Other products containing iodine were formed at the same time, but no other alcoholic iodide could be isolated from them.

C. S.

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**Pure Normal Propyl Compounds.** By E. LINNEMANN (Ann. Chem. Pharm., clxi, 26—43).

*Propyl alcohol* is obtained by heating 50 grams of pure propyl benzoate with 50 grams of water and 100 grams of solid caustic potash by means of a water-bath in a flask connected with a reversed condenser, until the mass becomes solid, and gives a clear solution with twice its volume of water. By using more water or less potash the ether is not completely decomposed. Pure propyl alcohol boils at  $97.41^{\circ}$ , and has at  $15^{\circ}$  the sp. gr. 0.8066.

*Propyl benzoate* is a thick, colourless, refractive liquid, possessing hardly any smell at the common temperature, but its vapour is irritating and produces coughing. Boiling point,  $229.47^{\circ}$ ; sp. gr. at  $16^{\circ} = 1.0316$ .

*Propyl acetate* is a mobile liquid, smelling like acetic ether, and at the same time like fruit. Boiling point,  $101.98^{\circ}$ ; sp. gr. at  $15^{\circ} = 0.8992$ .

*Propyl propionate* has a faint but pleasant odour, like that of pears. Boiling point  $122.44^{\circ}$ ; sp. gr. at  $13^{\circ} = 0.8885$ .

*Propyl butyrate* smells like other butyric ether. Boiling point,  $143.42^{\circ}$ ; sp. gr. at  $15^{\circ} = 0.8789$ .

*Propyl iodide*, obtained by treating the pure alcohol with anhydrous hydriodic acid, is a mobile liquid, smelling like ethyl iodide, and boiling at  $102.2^{\circ}$ . Sp. gr. at  $16^{\circ} = 1.7610$ . On heating it with fuming hydriodic acid to  $150^{\circ}$  it is not changed, and when it is heated with 6 vol. of water to  $100^{\circ}$  for 24 hours, about 36 per cent. is converted into propyl alcohol and hydrogen iodide. By the action of silver oxide or mercuric oxide on a solution of the iodide in glacial acetic acid at  $100^{\circ}$ , a small quantity of propylene is formed, besides dipropyl ether, propyl acetate, and propyl alcohol. Not a trace of an isopropyl compound was formed in any of these decompositions. *Dipropyl ether* smells like common ether, and boils at  $82^{\circ}$ — $86^{\circ}$ . By the action of iodine monochloride\* on propyl iodide, *normal propyl chloride* is formed, a very mobile liquid, boiling at  $46.36^{\circ}$ , and having the sp. gr. 0.9160 at  $18^{\circ}$ . The same compound was prepared from fermentation alcohol, by heating the iodide with mercuric chloride for three hours to  $130^{\circ}$ — $140^{\circ}$ ; it boiled at  $46.44^{\circ}$ , and had the sp. gr. 0.8959 at  $19^{\circ}$ .

*Propyl bromide* cannot be obtained by heating the iodide with cupric bromide. To prepare it, the fermentation alcohol was heated with concentrated hydrobromic acid. It smells like ethyl bromide, boils at  $70.82^{\circ}$ , and has the sp. gr. 1.3577 at  $16^{\circ}$ .

*Monobromopropyl bromide* is formed by heating together in closed tubes 5 grams of propyl bromide and 6.5 grams of bromine for four hours to  $130^{\circ}$ — $140^{\circ}$ . It boils at  $141.61^{\circ}$ , and has at  $17^{\circ}$  the sp. gr. 1.9463. In contact with acetic acid and zinc it yields propylene. On heating it with 6 vol. of water to  $200^{\circ}$  for six hours, it is decomposed, hydrobromic acid and acetone being formed. From these reactions it appears that this compound is identical with propylene dibromide,

\* This compound was obtained by melting together equal molecules of iodine and iodine trichloride, as a dark reddish-brown liquid, solidifying at a low temperature to large, thick prismatic crystals, melting at  $+ 17^{\circ}$ .

which compound is also formed by acting with bromine on isopropyl bromide (*Ann. Chem. Pharm.*, cxxxvi, 36).

C. S.

### Conversion of Normal Propyl Alcohol into Isopropyl Alcohol.

By E. LINNEMANN (*Ann. Chem. Pharm.*, cli, 43—70).

NORMAL propyl iodide was obtained from the fermentation alcohol, and had the boiling point  $102.25^{\circ}$ . 8 grammes of this iodide and 10 of dry silver cyanide are heated on the water-bath for one hour; the dry yellow product is quickly mixed with 20 grammes of finely powdered caustic potash, transferred to a combustion tube, and heated until the potash begins to melt; the alkaline vapours are absorbed by hydrochloric acid, and the product evaporated to dryness and extracted with alcohol to separate small quantities of ammonium chloride. About 68 per cent. of the theoretical yield of propylamine is thus obtained.

The hydrochloride melts at  $155^{\circ}$ — $158^{\circ}$ ; thus obtained it is perfectly pure, yielding with caustic potash a base distilling perfectly at  $46^{\circ}$ — $46.5^{\circ}$ , the corrected boiling point being  $49^{\circ}$ . Treated in quantities of 14 grams at a time with 30 of dry silver nitrite and 300 of water it yields an aqueous distillate from which the alcohol is obtained in the ordinary way. The crude alcohol contains *nitrosodipropylamine*, formed by the reaction—



but whether the propyl-radical in this is normal or iso- is not determined. It is separated from the alcohol by distillation on the water-bath. The yield of alcohol is between 40 and 50 per cent. of the theoretical amount, the nitrosodipropylamine being from 6 to 10 per cent. of the propylamine hydrochloride employed.

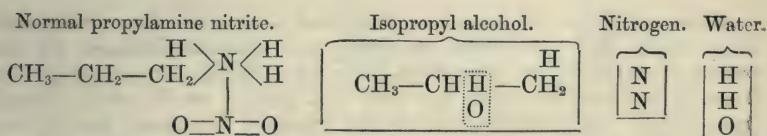
By the action of gaseous hydriodic acid on the alcohol dried by potash, isopropyl iodide is obtained in quantity, representing about 25 per cent. of the original normal iodide. Dehydrated by phosphoric anhydride it boils at  $89^{\circ}$ — $91^{\circ}$ , a portion remaining behind and not coming over below  $98^{\circ}$ ; this probably contains normal iodide. Heated with mercury chloride to  $110^{\circ}$ — $120^{\circ}$ , the principal portion boiling at  $89^{\circ}$ — $91^{\circ}$  furnished isopropyl chloride, distilling for the most part below  $39^{\circ}$ ; this chloride yields the alcohol by simply heating with 8—10 times its volume of water for 24 hours to  $100^{\circ}$ . Sometimes a portion of chloride remains unacted on and undissolved by the water. The aqueous solution, carefully freed from undecomposed chloride, is dehydrated by potash, and the alcohol allowed to flow slowly on to perfectly dry calcium chloride carefully cooled. The crystalline compound thus formed is kept over sulphuric acid *in vacuo* till no trace of isopropyl ether is perceptible by the smell, and decomposed with water. The separated alcohol is dried by potash, and finally over caustic baryta in a horizontal sealed tube in the water-bath. The boiling point (corrected) is then  $82.85^{\circ}$  under 725 mm. pressure. Sp. gr. = 0.7876 at  $16^{\circ}$ .

Saturated with gaseous hydriodic acid, this purified alcohol gives an iodide boiling at  $88.7^{\circ}$ — $89.5^{\circ}$  (corrected). Like the chloride and bro-

vide it is decomposed by heating with 8—12 volumes of water for 48 hours to 100°. In these respects the isopropyl compounds resemble those of trimethyl carbinol.

*Isopropyl benzoate* when heated splits up into benzoic acid and propylene. The ether is obtained by heating a dilute ethereal solution of isopropyl iodide with silver benzoate, and is an oily syrup insoluble in water.

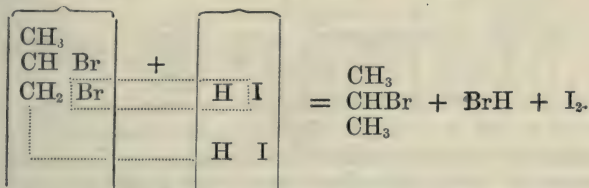
The production of isopropyl alcohol, instead of the normal alcohol, by the decomposition of normal propylamine nitrite is accounted for by the following scheme, whereby it appears that propylene is first formed, and then takes up  $\text{H}_2\text{O}$ .



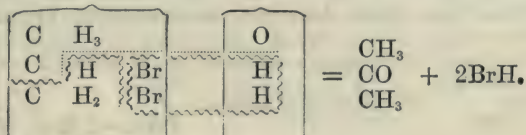
*Action of Nascent Hydrogen on Propylene Bromide.*—Propylene bromide was obtained by acting on allyl iodide with granulated zinc in presence of glacial acetic acid. The evolved propylene converted into bromide, fractionally distilled several times after dehydration by phosphoric anhydride and freed from traces of iodine-compounds by exposure to light in contact with strips of silver for several weeks, was found to have the corrected boiling point 141.61°, and the specific gravity 1.9463 at 17.5°.

Nascent hydrogen from granulated zinc and glacial acetic acid forms neither propyl bromide, isopropyl bromide, nor propyl hydride, as might be expected, but solely *propylene*; monobromopropylene bromide similarly yields *monobromopropylene*.

*Action of Hydriodic Acid on Propylene Bromide.*—Slightly fuming hydriodic acid and  $\frac{1}{4}$  its volume of bromide at 150° for 96—100 hours form principally isopropyl bromide; thus—



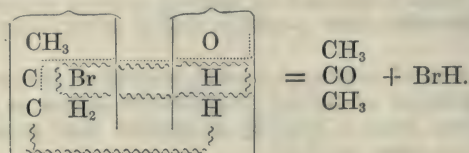
*Action of Water on Propylene Bromide.*—5 volumes water and 1 of bromide heated to 170°—180° for six hours form acetone as principal product, and also substances of higher boiling point, probably formed by the action on the acetone of the liberated hydrobromic acid—





The acetone thus obtained distilled between  $56^{\circ}$  and  $59^{\circ}$ .

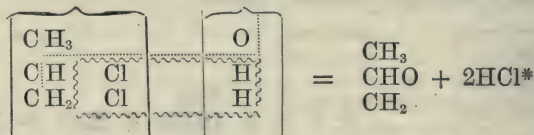
Monobromopropylene, obtained by the action of potash solution on propylene bromide, reacts with water in the same way, and does not form propyl aldehyde—



*Action of Nascent Hydrogen on Propylene Chloride.*—Zinc and glacial acetic acid have no action on propylene chloride obtained by the action of chlorine on propylene from allyl iodide, or on propylene from propylene dibromide by zinc and glacial acetic acid. Freed from higher chlorinated products by repeated fractional distillation, the chloride boils at  $96.82$  (corrected), and has the specific gravity  $1.1656$  at  $14^{\circ}$ .

*Action of Hydriodic Acid on Propylene Chloride.*—This action is precisely analogous to that on the bromide, isopropyl chloride being formed. This chloride distils at  $36^{\circ}$ — $37^{\circ}$  under  $730$  mm. pressure, and furnishes isopropyl alcohol when heated with six volumes of water to  $100^{\circ}$  for 24 hours.

*Action of Water on Propylene Chloride.*—Like the bromide, propylene chloride forms acetone; but, in addition, propyl aldehyde is produced, which is not the case with the bromide. By treatment of the portion of the product which distilled at  $56^{\circ}$ — $62^{\circ}$  with silver oxide, silver propionate was produced. The acetone obtained from this portion, after oxidation of the aldehyde, distilled at  $56^{\circ}$ — $58.5^{\circ}$ , and gave a crystalline double compound with acid sulphite of sodium. The author represents the production of propyl aldehyde thus—

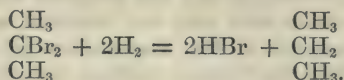


Monochloropropylene similarly forms acetone by the action of water.

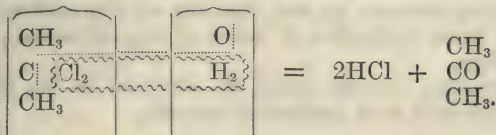
*Experiments with Methylbromacetol and Methylchloracetol.*—These substances were obtained respectively by the action of  $\text{PBr}_2\text{Cl}_3$  and  $\text{PCl}_5$  on acetone. The latter had the corrected boiling point  $69.69^{\circ}$  and the sp. gr.  $1.827$  at  $16^{\circ}$ . Methylchloracetol and nascent hydrogen have no action, whether the solution be acid or alkaline. Methylbromacetol, on the other hand, with zinc and glacial acetic acid, forms a gaseous hydrocarbon which does not combine with bromine and is

\* *Note by Abstractor.*—This reaction represents propyl aldehyde as a homologue of vinyl alcohol  $\begin{array}{c} \text{CH}_3\text{OH} \\ \parallel \\ \text{CH}_2 \end{array}$ , and not of ethyl aldehyde,  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CHO} \end{array}$ .—C. R. A. W.

readily soluble in alcohol. Without doubt it is propyl hydride, formed thus—



Methylchloracetol and water at 130°—140° are unaltered, but at 160°—180° for 30 hours produce acetone; aqueous hydriodic acid at 130°—140° for six hours also forms acetone, recognised in each case by its properties and formation of crystals with acid sulphite of sodium.



The production of propyl hydride from methylbromacetol affords a means of passing from the isopropyl to the normal propyl series, normal propyl chloride being obtainable from the hydride (Schorlemmer, *Ann. Ch. Pharm.*, 150, 209).

C. R. A. W.

### Simultaneous Distillation of Water and Butyl Iodide. By IS. PIERRE (*Compt. rend.*, lxxiv, 224).

WHEN water and butyl iodide (boiling point 122.5°) are heated in a retort, they distil over together at a constant temperature of 95° or 96°, the distillate containing 79 pts. of iodide to 21 of water, whatever be the proportions of the two in the retort. During the distillation, bubbles of vapour are seen to rise from the junction of the two layers of liquid, each bubble carrying up with it a drop of iodide.

Ethyl iodide (boiling point 70°) exhibits the same phenomena, the mixture boiling at 66°, but giving only 3 or 4 per cent. of water in the distillate.

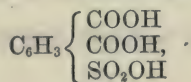
C. G. S.

### Tri-substitution Derivatives of Benzene. By MAX ASCHER (*Ann. Ch. Pharm.* clxi, 1—14).

JUST as the *di*-substitution derivatives of benzene are referred to the three isomeric *dicarbo*-acids, so might the *tri*-derivatives be referred to the three *tri-carbo*-acids; but as the constitution of only one of these is known, viz., trimesic acid, which, by reason of its formation from mesitylene contains the carboxyl groups in the positions 1 : 3 : 5, it becomes necessary to ascertain which of the two remaining members, hemi- and tri-mellitic acids, is a 1 : 3 : 4, and which a 1 : 2 : 3 derivative.

This the author has sought to do by replacing hydrogen in terephthalic acid (1 : 4) by SO<sub>3</sub>H, and this in its turn by COOH.

Terephthalic acid was converted into mono-sulpho-acid,



by heating it with strongly fuming sulphuric acid in sealed tubes to  $200^{\circ}$ ; from this acid the potassium salt was prepared and fused with sodium formate, but terephthalic acid only was obtained, so that either the tri-carbo-acid is decomposed at the temperature of the reaction, or the hydrogen evolved from the formate replaces the group  $\text{SO}_3\text{H}^*$ .

Attempts to prepare a tricyanide from dibromobenzene-sulphonic (last volume, ix, 1055) acid were also without result. The above method of attack proving unsuccessful, the author instituted experiments to prepare a dioxybenzoic acid of known constitution. The acid obtained has already been described in this Journal (p. 1055 of last volume); it only remains to add that the air-dry acid melts at  $148^{\circ}$ , and contains three molecules of water of crystallisation; its barium salt is anhydrous.

No corresponding cyanide could be obtained by the distillation of toluenesulphonic acid with potassium cyanide.

H. E. A.

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**Dibromopseudocumene.** By P. JANNASCH and H. SÜSSENGUTH (Zeitschr. f. Chem. [2], vii, 454).

ON brominating pseudocumene (from coal-tar oil) and subsequently distilling the crude product, the distillate between  $250^{\circ}$ — $290^{\circ}$  was observed to solidify entirely. On fractioning these crystals, a product boiling constantly and unchanged between  $276^{\circ}$ — $279^{\circ}$  was soon obtained, which was further purified by pressure and crystallisation from alcohol. The needles thus formed are of the composition  $\text{C}_9\text{H}_{10}\text{Br}_2$ , and are scarcely to be distinguished by their external appearance from Fittig's dibromomesitylene (*Ann. Ch. Pharm.* 147, 10); the melting and boiling points, however, are somewhat different—respectively  $63^{\circ}$ — $64^{\circ}$  and  $277^{\circ}$ — $278^{\circ}$ —so that the compound obtained is doubtless a dibromotrimethylbenzene isomeric with Fittig's dibromomesitylene.

H. E. A.

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**On the Production of Cymene from Hydrate of Turpentine-oil.** By PH. BARBIER (Compt. rend., lxxiv, 194).

THE author, remarking that camphor with phosphoric chloride yields chlorinated compounds which furnish cymene by distillation, applies a similar process to turpentine. Crystallised terpin,  $\text{C}_{10}\text{H}_{20}\text{O}_2 + \text{H}_2\text{O}$ , treated with two atoms of bromine, gives a yellowish semi-fluid body, apparently a brominated derivate from terpinene bromhydrate, decomposed on distillation into bromhydric acid and cymene. The latter, purified by caustic potash, is a mobile colourless liquid, having a penetrating odour of lemons, a boiling point of  $176^{\circ}$  to  $179^{\circ}$ , and a sp. gr. at  $15^{\circ}$  of 0.864. Fuming nitric acid dissolves it with formation of an insoluble nitrated body; warm sulphuric gives with it a conjugated sulpho-acid; bromine gives brominated compounds. Analysis: 89.54 carbon; 10.51 hydrogen.

C. G. S.

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\* Similarly, Barth obtained isophthalic acid from potassium disulphobenzoate and formate.



**Synthesis of a New Phenol.** By E. PATERNO (*Gazzetta Chimica Italiana*, i, 589—590).

THE author has applied Zincke's (*Deut. Chem. Ges. Ber.*, iv, 298) method of acting on benzene with benzyl chloride in presence of metals to anisol. The latter when heated with benzyl chloride and granulated zinc, evolves hydrochloric acid abundantly, and yields a liquid from which a limpid oil, boiling at about  $300^{\circ}$  may be separated by rectification. It is heavier than water, and has the formula  $C_{14}H_{14}O$ , or  $C_6H_5-CH_2-C_6H_5.O.CH_3$ .

The author regards it as the methylic ether of a new phenol, a view confirmed by its yielding methyl iodide when heated to  $150^{\circ}$  with hydriodic acid, together with an oil which dissolves in potash with green colour, and, when purified by distillation, crystallises in large plates. This, which is probably the new phenol, appears also to be produced by heating benzyl chloride and ordinary phenol with zinc.

C. E. G.

**Dinitrophenols.** By W. SCHNEIDER (*Zeitschr. f. Chem.* [2], vii, 452).

THE author has observed that volatile mononitrophenol yields, when nitrated, two dinitrophenols, viz., ordinary dinitrophenol and an isomeric melting at  $61^{\circ}$ — $62^{\circ}$ . The latter is more soluble in water than the former, and characteristic differences exist between the salts of the two nitro-compounds. The barium salt,  $[C_6H_3(NO_2)_2O]_2Ba + aq.$ , crystallises in long, pale-yellow needles, difficultly soluble in cold water.

H. E. A.

**Quinone Derivatives of Naphtol.** By E. LUDWIG (*Deut. Chem. Ges. Ber.*, iv, 970).

A SHORT notice of the fact that aqueous or alcoholic ammonia reacts on oxynaphthoquinones, exchanging  $NH_2$  for  $OH$ , e.g., oxynaphthoquinone,  $C_{10}H_5.O_2.OH$ , yields amido-naphthoquinone,  $C_{10}H_5.O_2.NH_2$ .

C. R. A. W.

**Nature of the Coal-tar Products Boiling between  $161^{\circ}$ — $169^{\circ}$ .**

By PAUL JANNASCH (*Zeitschr. f. Chem.* [2], vii, 453).

CRUDE coal-tar oil of high boiling point, entirely freed from phenol by treatment with alkali, gave, after repeated distillation, off sodium, two distillates boiling constantly between  $161^{\circ}$ — $165^{\circ}$  and  $165^{\circ}$ — $169^{\circ}$ , which, when acted upon by bromine in the cold, yielded compact monoclinic plates of unusual size and beauty, of the composition,  $C_8H_6Br_2O$ . These melt at  $68^{\circ}$ — $69^{\circ}$ , but are decomposed on distillation; they are also decomposed on boiling with alcohol, and even on exposure to the air; by nitric acid they are converted into picric acid. By the action of sodium amalgam, a highly crystalline monobrominated

product was obtained, which melts at  $38^{\circ}$ — $39^{\circ}$ , and distils unchanged at  $212^{\circ}$ — $216^{\circ}$ .

H. E. A.

**Action of Lead Iodide on some Metallic Acetates.** By

D. TOMMASI (Compt. rend., lxxiv, 125).

IODIDE of lead, in reacting upon the metallic acetates, gives rise to various reactions, according to the nature of the acetate which has been employed. Potassium acetate combines directly with lead iodide, but the acetates of copper and mercury produce double decomposition. Solutions of the acetates of sodium, ammonium, calcium, barium, magnesium, zinc, iron, aluminium, and some others, exert only a solvent action upon the iodide.

J. W.

**On Valerianic Acid from various Sources.** By E. ERLÉNMEYER and C. HILL (Ann. Ch. Pharm., clx, 257—303).

*Isobutyl-formic acid*,  $\begin{matrix} \text{CH}_3 \\ \diagup \\ \text{CH}_3 \end{matrix} \text{CH}-\text{CH}_2-\text{CO}-\text{OH}$ , was obtained by the action of alcoholic potash on isobutyl cyanide prepared from fermentation butyl alcohol, by conversion into iodide and treatment with potassium cyanide; the iodide employed was prepared from alcohol of B. P.  $103^{\circ}$ — $105^{\circ}$ ; it boiled at  $117.5^{\circ}$ — $118^{\circ}$  (uncorrected) at 715 mm., and had the sp. gr. 1.6433 at  $0^{\circ}$ , its expansion being given by the formula—

$$V = 1 + 0.00094701 t + 0.000002651 t^2 - 0.0000000052 t^3.$$

The cyanide boiled at  $126^{\circ}$ — $128^{\circ}$  at 714 mm., and had the sp. gr. 0.8226 at  $0^{\circ}$ , its expansion being given by the formula—

$$V = 1 + 0.00095951 t + 0.000004292 t^2 - 0.00000001449 t^3.$$

The acid boiled at  $171^{\circ}$ — $172^{\circ}$  at 722.5 mm. (uncorrected), and had the sp. gr. 0.9468 at  $0^{\circ}$ , its expansion being given by the formula—

$$V = 1 + 0.0009467 t + 0.0000010276 t^2 + 0.00000000299 t^3.$$

It had no action on polarized light, and formed a silver salt readily soluble in hot water, but only sparingly in cold; 100 parts of water at  $21^{\circ}$  dissolved 0.185 parts; the barium salt crystallises anhydrous, its solution being partially decomposed, forming baryta and free acid on standing and especially on boiling; 100 parts of the solution contain 49 parts of the salt at  $22^{\circ}$ .

*Valerianic acid from valerian root* was found to contain small quantities of formic and acetic acids and an acid of B. P.  $180^{\circ}$ — $185^{\circ}$ , but no butyric acid; when purified by fractional distillation it boiled constantly at  $171^{\circ}$ — $173^{\circ}$  at 718.3 mm., and had the sp. gr. 0.9462 at  $0^{\circ}$ , and the rotatory power  $+5.0$  for 50 cm., its expansion being given by the formula—

$$V = 1 + 0.00093415 t + 0.000001235 t^2 + 0.00000000198 t^3.$$

By recrystallisation of the barium salt an optically inactive acid was obtained. Its silver and barium salts resemble those of isobutyl-formic acid, save that the latter is slightly less soluble. After purification by several recrystallisations, 100 parts of the solution contained 46 parts at 18°, 44 parts at 16°; 100 parts of water dissolved 0.186 parts of silver salt.

*Valerianic acid from amylic alcohol.*—By conversion into barium sulphamylate and crystallisation three products were obtained: difficultly soluble crystals, readily soluble crystals, and mother-liquors of soluble crystals; by reconversion into alcohol and oxidation these two last products gave acids which appeared to be identical, giving silver salts that yielded correct numbers on analysis, the alcohols having respectively the rotatory powers  $-20^{\circ}$  to  $-21^{\circ}$  and  $-22^{\circ}$  to  $-23^{\circ}$ . The alcohol from the soluble barium salt distilled principally between  $125^{\circ}$  and  $127.5^{\circ}$ , but a considerable portion only distilled at  $127.5^{\circ}$ — $130^{\circ}$ ; by oxidation with chromic acid solution it yielded an acid distilling for the most part at  $168^{\circ}$ — $171^{\circ}$ , and having a rotatory power of  $+39^{\circ}$  to  $40^{\circ}$ ; its silver salt is somewhat more soluble than that of isobutyl formic acid, 100 parts of water dissolving 0.195 parts at  $22^{\circ}$ ; its barium salt does not crystallise, and is apparently miscible with water in all proportions; it is not a colloid, however, as it readily dialyses through parchment paper. Its sp. gr. was 0.8244 at  $0^{\circ}$ ; its expansion being given by the formula—

$$V = 1 + 0.00085560 t - 0.0000013306 t^2 + 0.000000034167 t^3.$$

where the value of the first constant is sensibly different from that of the other acids described above, and that of the second constant is negative.

The acid from the insoluble barium sulphamylate boiled at  $171.5^{\circ}$  at 721.8 mm.; it gave a feeble rotation 1.0 to 1.5 for 50 cm., but on recrystallisation of its barium salt an acid destitute of rotatory power was obtained. Its sp. gr. was 0.9465 at  $0^{\circ}$ , its expansion being given by the formula—

$$V = 1 + 0.00094228 t + 0.0000011342 t^2 + 0.00000000259 t^3.$$

the alcohol from which it was formed boiled at  $129^{\circ}$ — $130.1^{\circ}$  at 714.8 mm. (corrected), and had a feeble but distinct rotatory action, its sp. gr. being 0.8244 at  $0^{\circ}$ .

After several recrystallisations, the silver and barium salts of this acid corresponded perfectly in properties and solubility with those from isobutyl cyanide and valerian root; 100 parts of water dissolved 0.185 of the silver salt at  $20.5^{\circ}$ ; 100 parts of solution contained 48.4 of barium salt at  $18^{\circ}$ ; 48.7 parts at  $19^{\circ}$ ; in aqueous alcohol and absolute alcohol the solubilities of the three acids showed the same identity, viz., 14.6, 13.9, and 14.4 parts in 100 of solution in aqueous alcohol; 3.3, 2.7, and 3.5 in 100 of solution in absolute alcohol.

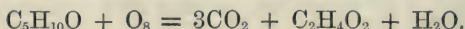
*Valerianic acid from leucine* was difficult to purify; the principal portion distilled between  $168^{\circ}$ — $171^{\circ}$ ; its rotatory power was  $+17$  for 50 cm.; its silver salt and barium salt resembled those of the active acid from amylic alcohol, the latter refusing to crystallise; 100 parts of solution contained 0.191 of silver salt at  $21^{\circ}$ , 0.189 at  $20^{\circ}$ .



Attempts to obtain the active acid in a pure state by crystallisation of the sulphamylate, &c., by fractional oxidation of fermentative alcohol and by fractional distillation proved abortive; a residue in the fabrication of valerianic acid, however, was found to contain considerable quantities of an amyl valerate, from which an acid was obtained which had the rotatory power  $+48.7^\circ$  for 50 cm; this was carefully compared with pure inactive acid, and was found to begin to boil at  $170^\circ$ , the temperature soon rising to  $172.5^\circ$  and finally to  $173.5^\circ$ ; the inactive acid, examined with the same thermometer, &c., began to boil at  $173.5^\circ$ , the temperature immediately rising to  $174.5^\circ$ , and remaining constant at that point; the active acid had sp. gr. 0.9505 at  $0^\circ$ , its expansion being given by the formula—

$$V = 1 + 0.00094311 t + 0.0000016147 t^2 - 0.000000001458 t^3.$$

This active acid was oxidised by a mixture of 2 vols. water and 1 vol. sulphuric acid saturated with potassium dichromate;  $\text{CO}_2$  was produced to the extent of 93.7—102.8 per cent. of the acid used, and simultaneously acetic acid; on similarly treating the inactive acid,  $\text{CO}_2$  was evolved to the extent of 120.4—123.4 per cent., and acetic acid also produced; no other products being formed in either case; hence the latter splits up in accordance with the equation—



which requires 129.3 per cent. of  $\text{CO}_2$ .

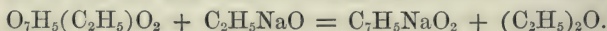
The authors conclude that the inactive acid from fusel-oil alcohol, valerianic acid from valerian, that from isobutyl cyanide, and the isopropacetic acid of Frankland and Duppa are identical, being represented by the formula  $\begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix} \text{>CH-CH}_2\text{-CO-OH}$ ; while the active acid from fusel-oil alcohol (and that from leucine?) is methyl-ethacetic acid,  $\begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix} \text{-CH}_2\text{-CH-CO-OH}$ , more or less pure.

C. R. A. W.

### Action of Sodium Alcoholate on Benzoic Ether. By

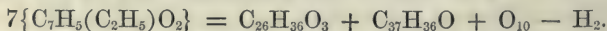
A. GEUTHER (Jenaische Zeitschrift, vii, 126—129).

THE author refers to former researches which showed that the action of sodium alcoholate upon benzoic ether may be thus represented:



Besides these products, there are formed three other substances, two oily bodies, and the third of an acid nature. These three the author has now investigated. He finds the acid to be formic acid, while to the first of the oily substances he gives the formula  $\text{C}_{26}\text{H}_{36}\text{O}_3$ , or perhaps  $\text{C}_{26}\text{H}_{34}\text{O}_3$ , and to the second the formula  $\text{C}_{37}\text{H}_{36}\text{O}$  is assigned.

The following equation may represent the reaction—



these 10 parts of O thus liberated may react on the benzoic ether so as give formic acid.

M. M. P. M.

**Bromobenzenesulphonic Acid.** By R. FITTIG (Zeitschr. f. Chem. [2], vii, 449).

By the action of bromine on benzenesulphonic acid, A. Ross Garrick obtained a bromobenzenesulphonic acid, the salts of which were found on comparison to differ from those of Couper's acid prepared from bromobenzene and sulphuric acid. The latter gave also resorcin on fusion with potassic hydrate, whereas Garrick could not obtain a well characterised product from his acid by similar treatment; certain reactions, however, pointed to the formation of hydroquinone. The behaviour of this isobromobenzenesulphonic acid with potassic hydrate has therefore been re-examined by H. Wölz, who obtained an oily product, exactly as described by Garrick, only partially soluble in water; the aqueous solution left on spontaneous evaporation a dark coloured crystalline residue from which, by sublimation, pure *resorcin* was obtained. Pure hydroquinone was ascertained to give no trace of its isomerides when similarly sublimed, nor was it altered by fusion with potassic hydrate, so that the resorcin cannot have been a product of the conversion of hydroquinone.

Further, potassium isobromobenzenesulphonate was distilled with potassium cyanide, whereby a liquid and a solid product were obtained; the former gave benzoic, the latter *terephthalic* acid on treatment with alkali. The results obtained with potassic hydrate and with potassium cyanide are, therefore, in complete accordance, and necessitate a re-examination of the two series of salts.

H. E. A.

**Notice on Amidobenzene-sulphonic Acids.** By L. PRATESI (Deut. Chem. Ges. Ber., iv, 970).

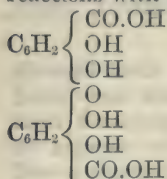
THE mixture of isomeric acids obtained from phenol and sulphuric acid gives a crystalline compound with aniline soluble in water and alcohol. This, when free from sulphuric acid, and cautiously heated, gives off phenol, aniline, and sulphurous acid, and forms a non-volatile crystalline product,  $C_6H_4 \begin{Bmatrix} NH_2 \\ SO_3H \end{Bmatrix}$  isomeric with Laurent's sulphanilic acid, and apparently identical with the sulphanilic acid of Gerhardt, Hofmann, Buckton, and Schmitt.

C. R. A. W.

**On Tannic Acid, and Derivatives therefrom.** By HUGO SCHIFF (Deut. Chem. Ges. Ber. iv, 967).

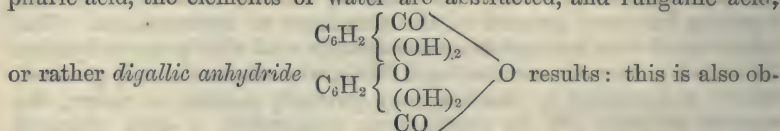
LÖWE's production of tannic acid by the action of arsenic acid on gallic acid is verified. A minute quantity of arsenic acid suffices for the conversion of considerable quantities of gallic acid, without any production of ellagic acid; this latter is formed only by heating the *dry* substances to 120°–160°, the arsenic acid being reduced to arsenious. Analyses of the lead salts,  $C_{14}H_6Pb_2O_9 + 2H_2O$  and  $C_{14}H_4Pb_3O_9$ , and the production of *tetracetyl tannic acid*  $C_{14}H_6(C_2H_3O)_4O_9$  (which gives no colour

reactions with ferric chloride), show that the product is *digallic acid*,



. When digallic acid is heated to  $70^\circ$ — $80^\circ$  with sul-

phuric acid, the elements of water are abstracted, and *rufigallic acid*,



tained from gallic ether, triacetyl-gallic ether, and tetracetyl-tannic acid: it yields a tetracetyl derivative,  $\text{C}_{14}\text{H}_4(\text{C}_2\text{H}_3\text{O})_4\text{O}_8$  crystallisable from boiling glacial acetic acid. From the reduction of arsenic to arsenious acid in the production of ellagic acid, the author considers the formula  $\text{C}_{14}\text{H}_6\text{O}_8$  hitherto attributed to the latter to be erroneous. This formula represents its anhydride, the acid itself being  $\text{C}_{14}\text{H}_8\text{O}_9$ , derived from gallic acid by abstraction of hydrogen: with ferric chloride it gives the phenol reaction.

Triacetyl-gallic ether  $\text{C}_7\text{H}_2(\text{C}_2\text{H}_3\text{O})_3(\text{C}_2\text{H}_5)\text{O}_5$  does not give the iron reaction, and does not precipitate lead salts, whereas gallic ether gives a deep blue with ferric chloride, and forms the salt  $\left. \begin{array}{l} \text{C}_7\text{H}_2(\text{C}_2\text{H}_5)\text{O}_5 \\ \text{C}_7\text{H}_2(\text{C}_2\text{H}_3\text{O})_5 \end{array} \right\} \text{Pb}_3$ .

Salicylic acid gives condensation-products with phosphoryl chloride.

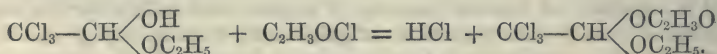
When  $\text{H}_2\text{O}$  is removed, *salicylide*  $\text{C}_7\text{H}_4\text{O}_2$  crystallisable from alcohol results; when  $3\text{H}_2\text{O}$  are abstracted from 4 molecules of acid, *tetrasalicylide*  $\text{C}_{28}\text{H}_{16}\text{O}_9$  is formed as a solid resin. Salicylic aldehyde gives an uncrystalline purple-red condensation-product, soluble in alkalies, with the production of a beautiful violet colour.

C. R. A. W.

**On Chloral.** By VICTOR MEYER and L. DULK (Deut. Chem. Ges. Ber. iv, 963).

In order to decide whether chloral hydrate is a true diatomic alcohol (ethylideneglycol)  $\text{CCl}_3 - \text{CH}(\text{OH})_2$ , or merely a compound containing water of crystallisation  $\text{CCl}_3 - \text{COH} + \text{H}_2\text{O}$ , the action of acetyl chloride was tried with the result of producing, not diacetyl-chloral hydrate, but *tetrachlorinated acetic ether*  $\text{CCl}_3 - \text{CHCl} - \text{O} - \text{C}_2\text{H}_3\text{O}$ .

Chloral alcoholate, however, yields *acetylchloral alcoholate*, in accordance with the equation—



This result is in favour of the view which regards chloral-alcoholate as the ethylic ether of ethylidene-glycol, and therefore chloral-hydrate as that glycol itself.



Thus obtained, and purified by repeated fractional distillation, acetyl-chloral alcoholate, is a colourless transparent oil of a peculiar smell, boiling constantly at  $198^{\circ}\text{C}$  (uncorrected), and of sp. gr. 1.327 at  $11^{\circ}\text{C}$ . Boiling concentrated potash solution does not attack it.

When perfectly anhydrous chloral and acetic anhydride are heated together to  $150^{\circ}$  in molecular proportions, they unite, forming *diacetyl chloral hydrate*  $\text{CCl}_3\text{—CH} \begin{smallmatrix} \text{O.C}_2\text{H}_3\text{O} \\ \text{O.C}_2\text{H}_3\text{O} \end{smallmatrix}$ ; this boils constantly at  $221^{\circ}\text{—}222^{\circ}$  (uncorrected), has a sp. gr. of 1.422 at  $11^{\circ}$ , is not miscible with water, and is not attacked by cold potash-solution, though on heating it, the odour of chloroform is perceptible; it is evidently *trichlorinated diacetate of ethylidene-glycol*, the diacetate itself being similarly obtained by heating aldehyde and acetic anhydride to  $180^{\circ}$  (Geuther, *Ann. Ch. Pharm.* 106, 249).

Chloral and anhydrous trimethylamine combine, forming a solid substance crystallisable from water, alcohol, or ether, in large shining prisms that melt at  $46^{\circ}\text{—}48^{\circ}$ : this and other compounds with other aldehydes and trimethylamine, are reserved for further investigation.

C. R. A. W.

### Action of Bromochloride of Phosphorus on Chloral. By

E. PATERNÒ (*Gazzetta Chimica Italiana*, i, 590—592).

THE author has shown (*Giornale di scienze naturali ed economiche*, v, 117) that the action of phosphorus pentachloride on chloral gives the compound  $\text{C}_2\text{HCl}_5$ , which he considers as a chlorinated derivative of dimethyl (or pentachlorethane), and he has now obtained the corresponding chlorobrominated derivative,  $\text{CCl}_3\text{CHBr}_2$ , by acting on chloral with phosphorus chlorobromide.

The latter was prepared by dropping bromine into well-cooled phosphorus trichloride; it crystallises in long prismatic needles of a fine red colour, which melt at the ordinary temperature to a red liquid. The addition of chloral to this compound gives rise to a slight manifestation of heat, the reaction being completed by boiling the mixture for a few minutes. On addition of water, an oil separates, which, when dried and submitted to fractional distillation under diminished pressure, yields the compound  $\text{C}_2\text{HCl}_3\text{Br}_2$  as a colourless, transparent, highly refracting liquid, of sp. gr. 2.317 at  $0^{\circ}$ . It has a pleasant odour, is insoluble in water, but readily soluble in alcohol and ether. It boils at about  $200^{\circ}$  with partial decomposition, but distils unchanged at  $93^{\circ}\text{—}95^{\circ}$  at a pressure of 14 millimeters.

Its refractive index for D at  $25.7^{\circ}$  is 1.52991. When treated with alcoholic potash, it is rapidly decomposed, with formation of potassium chloride, and an oily substance distilling at  $143^{\circ}\text{—}160^{\circ}$ , but apparently not homogeneous.

C. E. G.

### Note on the Transformation of Phenol into Alkaloids. By

DUSART and BARDY (*Compt. rend.*, lxxiv, 188—190).

THE conversion of phenol into phenylamine by caustic ammonia, was announced by Laurent and Hofmann, but has not been since confirmed.

Sterry Hunt in 1849 effected the reverse transformation by the action of nitrites. The authors, having recently proved that phenol combines with phenylamine hydrochloride, show in this paper that the action of phenol on ammonia hydrochloride will give phenylamine. 150 grm. phenol, 50 grm. ammonia hydrochloride and 25 grm. fuming hydrochloric acid (which much assists the reaction) are heated in a sealed tube for 30 hours to  $315^{\circ}$  C. The liquid, after removing the ammonia salt, is distilled with aqueous potash. The distillate, shaken with hydrochloric acid, gives an aqueous layer containing phenylamine, and an oily layer of phenyl chloride. The residue in the retort deposits crystals of diphenylamine. The last is the most abundant product, the phenylamine the least. In this reaction, phenyl chloride is first produced, and in the presence of ammonia hydrochloride gives phenylamine. The latter, acting on a fresh quantity of phenyl chloride, yields diphenylamine.

Berthelot obtained from methylic alcohol and ammonia hydrochloride at  $320^{\circ}$  a small quantity of aniline. The authors heat 2 pts. ammonia hydrochloride, 5 methylic alcohol, and 1 hydrochloric acid to  $207^{\circ}$  for 30 hours, and obtain oxide and chloride of methyl, and methylamine hydrochloride, amounting to one-third of the ammonium chloride used. From the lower temperature here required, they consider that methyl chloride is essential to the reaction, and that it must have been formed in Berthelot's process by dissociation of the ammonia hydrochloride.

C. G. S.

### Separation of the Two Isomeric Toluidines.

By A. ROSENSTIEHL (Compt. rend., lxxiv, 249—252).

CRYSTALLISED toluidine forms only an acid salt with oxalic acid, of the formula  $C_2H_2O_4 \cdot (C_7H_9N) \alpha \cdot H_2O$ , soluble at  $15^{\circ}$  in 125 pts. of water and 6660 pts. of pure ether. Pseudotoluidine forms two salts; the one acid,  $C_2H_2O_4 \cdot (C_7H_9N) \beta \cdot H_2O$ , soluble at  $18^{\circ}$  in 200 pts. of ether, the other neutral and anhydrous,  $C_2H_2O_4 \cdot 2(C_7H_9N) \beta$ , dissolving in 267 pts. of ether at  $18^{\circ}$ . When oxalic acid is added to a mixture of the two alkaloids, the toluidine is first saturated, forming the acid salt, and until this saturation is completed, the pseudotoluidine remains free. A similar reaction occurs when toluidine is added to neutral oxalate of pseudotoluidine, the latter being set at liberty: in this case a mixture of a neutral salt with an alkaloid gives *an acid salt*.

These properties render possible a volumetric estimation of the two isomerides. The author employs standard solutions of toluidine and of oxalic acid in ether free from alcohol. He dissolves 0.2 gram. of the alkaloid to be analysed in 80 grams of ether, and adds the oxalic solution from a burette. The precipitate of acid toluidine oxalate is at first granular, but near the end of the operation it becomes crystalline. The experiment is complete, when a drop of oxalic acid added to a little of the filtered liquid gives no crystalline precipitate. By the standard solution of toluidine the author ascertains that no excess of oxalic acid has been added. To prove that the precipitate is really toluidine salt, he washes with ether the crystals adhering to the glass, dries and dis-



solves them in bihydrated sulphuric acid; a splendid, but transient blue colour proves the presence of toluidine.

When the mixture contains only 5 per cent. of toluidine, the author adds all the oxalic acid at once, and after some hours washes, dries, and weighs the precipitate. The analyses give very correct results. In the presence of aniline, however, the precipitate is a mixture of aniline and toluidine oxalates.

C. G. S.

**On some Compounds of Aniline and Toluidine with Metallic Iodides.** By HERM. VOHL (Arch. Pharm. [2], cxlviii, 201—208).

In 1863 Hugo Schiff made some researches on the compounds of aniline with metallic salts, and assigned to these compounds formulæ representing that two atoms of hydrogen in two molecules of aniline were replaced by one atom of a dyad metal. Vohl does not consider that there is any reason why these products should not be merely double salts of aniline with the corresponding haloid metallic compounds. Some time since he prepared the compound of aniline with zinc chloride  $2(\text{C}_6\text{H}_7\text{N})\cdot\text{ZnCl}_2$ , and also the compound of this body with hydrogen chloride. In this salt there was absolutely no hydrogen eliminated, and it was therefore considered to be merely a double compound. The author has now prepared a series of compounds of analogous composition.

Zinc-iodide-aniline, prepared by mixing alcoholic aniline solution with a solution of zinc iodide in alcohol, forms brilliant colourless needles, soluble in alcohol, and having the composition  $2(\text{C}_6\text{H}_7\text{N}) + \text{ZnI}_2$ .

Cadmium-iodide-aniline, prepared in a similar manner to the zinc compound, and having an analogous composition, crystallises in large brilliant needles, soluble in alcohol.

Mercuric-iodide-aniline prepared as above, is a yellow crystalline substance, but loses aniline on crystallisation from spirit, and becomes of a dark red colour; this compound is analogous in composition to the above-named salts.

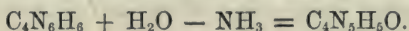
Zinc-iodide-toluidine,  $2(\text{C}_7\text{H}_9\text{N})\cdot\text{ZnI}_2$  crystallises in groups of needles easily soluble in alcohol.

A. P.

**Synthetical Researches on the Ureïds.** By O. JACOBSEN and A. EMMERLING (Deut. Chem. Ges. Ber., v, 947—956).

DRY ammonia and cyanogen gas combine, forming *hydrazulmin*,  $\text{C}_4\text{N}_6\text{H}_6$ , in amorphous, jet-black scales, which, when heated, first decrepitate violently, then swell up like Brodie's graphitic acid, giving out gases, and leaving a residue of paracyanogen, which completely volatilizes at a higher temperature.

Water acts on hydrazulmin, the following reaction taking place:—





*Hydrazulmoxin*,  $C_4N_5H_5O$ , is a brown amorphous mass, which dissolves but sparingly in water, more freely in presence of ammonia. When the ammoniacal solution is exposed to the air, the hydrazulmoxin separates out again gradually. This compound is identical with the so-called azulmic acid, which is formed by the spontaneous decomposition of an aqueous solution of cyanogen, and by the action of cyanogen on aqueous ammonia. The more concentrated the latter, the greater is the quantity of azulmic acid formed, whilst in more dilute solutions the formation of oxamide preponderates. A hot aqueous solution of azulmic acid exhibits a fine violet fluorescence; on heating it gently with caustic potash or concentrated sulphuric acid, yellowish-brown solutions are obtained, which, after cooling, show a dark green fluorescence.

When azulmic acid is boiled with water and the hot solution filtered, it separates out on cooling with a much lighter colour; and, by repeating this operation several times, a product is at length obtained, forming light yellow amorphous flakes. This body is identical with *mycomelic acid*,  $C_4N_4H_4O_2$ , which Liebig and Wöhler first obtained by the action of ammonia upon alloxan, and which Hlasiwetz afterwards prepared by heating uric acid and water together in sealed tubes to  $180^\circ$ . Mycomelic acid is formed according to the equation—



Mycomelic acid is soluble in boiling water; the solution shows a fine greenish-blue fluorescence.

By oxidising azulmic acid with potassium permanganate or nitric acid two atoms of hydrogen are replaced by oxygen and *azoxulmoxin*,  $2C_4N_5H_3O_2 + H_2O$  is formed, a reddish yellow, crystalline powder, insoluble in water, but readily soluble in concentrated sulphuric acid. This solution shows an intense light green fluorescence, like uranium glass.

The constitution of these different compounds is most probably as follows:—

Paracyanogen.	Hydrazulmin.	Azulmic acid.	Mycomelic acid.	Azoxulmoxin.
$  \begin{array}{c}  CN \\    \\  C \\    \\  C(N)''' \\    \\  C \\    \\  CN  \end{array}  $	$  \begin{array}{c}  CN \\    \\  NH_2 \\    \\  C(NH)'' \\    \\  C \\    \\  NH_2 \\    \\  CN  \end{array}  $	$  \begin{array}{c}  CN \\    \\  OH \\    \\  C(NH)'' \\    \\  C \\    \\  NH_2 \\    \\  CN.  \end{array}  $	$  \begin{array}{c}  CN \\    \\  OH \\    \\  C(NH)'' \\    \\  C \\    \\  OH \\    \\  CN.  \end{array}  $	$  \begin{array}{c}  CN \\    \\  OH \\    \\  C(NO)'' \\    \\  C \\    \\  NH_2 \\    \\  CN.  \end{array}  $
				C. S.

### Preparation of Crystallised Indigotin by Means of Phenol.

By C. MÉHU (J. Pharm. [4], xiv).

MÉHU finds in phenol an excellent solvent for indigotin. The hot phenol takes up indigotin and re-deposits most of it on cooling in the crystalline form, retaining enough to colour the acid deep blue. To prevent the solidification of the phenol during refrigeration, alcohol, camphor, or benzene may be added. 500 grams phenol served for the preparation of 2 grams of pure indigotin.

T. S.

**The relation between the Specific Gravity of Indigo and the amount of Colouring Matter present.** By G. LEUCHS (J. pr. Chem. [2], iv, 349—352).

As it is well known that the quality of indigo is judged of by its specific gravity amongst other properties, the author examined 49 specimens of indigo, containing from 24 to 60·5 per cent. of indigotine, with the object of ascertaining whether there was any definite relation between the specific gravity and the amount of colouring matter present. The tabulated results of the examination of 30 of these specimens shows *generally* that good indigo (56 to 56·5 per cent.) has a comparatively low specific gravity (1·324), whilst that of the poorer sorts increases as the amount of colouring matter becomes smaller, that of a specimen of 27 per cent. being 1·575.

C. E. G.

**On Indophan, a new Blue Colouring Matter derived from Naphthyl-purpuric Acid.** By E. v. SOMMARUGA (Chem. Centr., 1871, 617; Dingl. polyt. J., ccii, 276).

HLASIWETZ finds that when dinitronaphthol is converted by the action of potassium cyanide into naphthyl-purpuric acid, indophan, a blue substance similar to indigo, is formed at the same time.

According to the author, the best method of preparing pure indophan is the following:—30 grams of dinitronaphthol with about 2 litres of water are heated to boiling, and sufficient aqueous ammonia is added to ensure complete solution. Into this a hot concentrated solution of 45 grams potassium cyanide is dropped. In ten minutes the reaction is completed. The whole is now washed on the filter with boiling water till the filtrate ceases to become coloured. A violet-coloured mass is thus obtained having a beautiful green metallic lustre, and consisting of a mixture of free indophan and a potassium-compound of that body. Washed for a long time with boiling water, the latter becomes coloured from the solution of a trace of the compound; addition of potassium carbonate prevents this solution, and precipitates from the washings a brown impurity. The mass on the filter is now heated with very dilute hydrochloric acid, filtered and washed, till the filtrate is free from hydrochloric acid.

The pure dry substance is of a violet colour, and has a beautiful green metallic lustre.

The potassium and sodium compounds are obtained, by treatment with solution of potassium or sodium hydrate, filtering, and washing till all free alkali is removed. Both these compounds greatly resemble indigo. Indophan is insoluble in water, alcohol, ether, benzol, and carbonic disulphide, but moderately soluble in sulphuric acid and warm acetic acid, and slightly so in melted naphthalene. The solutions are purple-red; from these indophan cannot be obtained in a crystalline condition; it may, however, be sublimed like indigo. Nitric acid appears to oxidise it, forming a brown-red body, soluble in alkaline solutions. Indophan is not reducible by lime, and ferrous sulphate as indigo is. On warming it with alcoholic potash-solution, first a dark green body



is obtained, and by further action a humus-like substance is precipitated. Fused potassium hydrate gives the same decomposition products with this body as with naphthyl purpuric acid.

W. S.

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### The Decomposition of Albumin by Potassium Permanganate.

By H. TAPPEINER (J. pr. Chem. [2], iv, 408—412).

THE author has confirmed Städeler's and Loew's refutations of Béchamp's renewed assertion that urea is a product of the oxidation of albumin by potassium permanganate. The supposed urea was found to consist of crystals of barium nitrate contaminated with some organic matter, not urea. Further, but only preliminary, researches were made to ascertain what really are the products of the oxidation of albumin in the above manner. 20 grams of dry egg-albumin were treated on the water-bath with 200 grams of potassium permanganate and 500 c.c. water till complete discoloration had taken place. Methylamine and ammonia were developed. The manganese dioxide was filtered off, and the filtrate distilled in a retort after being rendered feebly acid with sulphuric acid. The acid distillate contained a mixture of the fatty acids. The residue in the retort was poured off from the crystals of potassium sulphate and exhausted with ether. This on evaporation left 0.7 gram of benzoic acid; the calcium salt was prepared from it and analysed. From the residue, insoluble in ether, oxalic acid and leucine were prepared, and the copper-compound of the latter. Now, since leucine in alkaline solution is oxidised by potassium permanganate into oxalic and valerianic acids, it must be supposed that the leucine was formed during the distillation with sulphuric acid by the splitting up of other bodies formed by a less perfect oxidation of albumin. In the mother-liquors from the leucine the presence of other introgenous products of decomposition was shown by the fact, that they yielded a considerable quantity of free nitrogen when treated with Knop's reagent, although no ammonia salts were present.

T. S.

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## Physiological Chemistry.

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### The Chemistry of Respiration, a Process of Dissociation. By

F. DONDERS (Pflüger's Archiv. für Physiologie, iv, 20—26).

IN this paper the author states that the process of respiration, restricting the term to the mutual interchange of  $\text{CO}_2$  and oxygen in the blood, is a process of dissociation, an opinion already expressed by Ludwig and Worm Müller. Dissociation is the separation of the molecules of a body into two or more simple molecules by the agency of heat alone, and a compound is in a state of dissociation when it is partly decomposed and partly remains undecomposed under exposure to a constant temperature. Thus, when calcium carbonate is heated *in vacuo* it just begins to be decomposed at  $440^\circ$  (dissociation temperature), and as



the temperature is raised, more and more of the salt is decomposed, and the tension of the carbon dioxide liberated is increased. The condition of equilibrium at any given temperature is attained when the tension of the carbon dioxide becomes so great that new molecules of it combine with the lime as fast as others are driven out by the heat. If they are removed as quickly as they are liberated, and then prevented from again combining with the lime, the calcium carbonate will be entirely decomposed. In a similar way the carbon dioxide is united in a condition of dissociation with some of the salts, and perhaps albuminous bodies of the blood, and the oxygen with oxyhæmoglobin. As the nitrogen obeys Dalton's law, it may be assumed to be in a state of true solution. In trying to determine the temperature at which dissociation begins in the blood, its amount as a function of tension and temperature, and the rapidity of its progress, he found that—

I. Oxygen was driven out of defibrinated blood saturated with it:

a. By hydrogen. Dissociation temperature is between  $0^{\circ}$  and  $1^{\circ}$ . At  $37^{\circ}$  hydrogen liberates more oxygen in 10 seconds than in 1000 at  $0^{\circ}$ .

b.  $\text{CO}_2$  drives out oxygen quicker at  $37^{\circ}$  than at  $0^{\circ}$ , and acts much more quickly than hydrogen. Diminution of oxygen with absorption of  $\text{CO}_2$  by the blood lessens tissue-change in it. At a high temperature  $\text{CO}_2$  decomposed hæmoglobin.

II. Defibrinated blood containing much  $\text{CO}_2$  is far more quickly arterialized by air free from  $\text{CO}_2$  at  $0^{\circ}$  than at  $37^{\circ}$ .

III. Hermann's statement that CO is not expelled from its combination with hæmoglobin by oxygen is incorrect. It is expelled from blood saturated with it by oxygen,  $\text{CO}_2$ , and hydrogen, even at  $0^{\circ}$ . Oxygen does not form  $\text{CO}_2$  with the CO, but drives it out as CO. Temperature has a great influence on the expulsion of CO by hydrogen, but less on its expulsion by oxygen.  $\text{CO}_2$  drives out CO more quickly at  $37^{\circ}$  and  $40^{\circ}$  than at  $0^{\circ}$ , but causes decomposition of hæmoglobin.

IV. Paraglobulin, precipitated from dilute serum by carbon dioxide is dissolved by passing hydrogen through the liquid, as well as by oxygen, but less readily. Solution occurs more readily at  $37^{\circ}$  than at  $0^{\circ}$ . Paraglobulin is probably a compound of  $\text{CO}_2$  and globulin, soluble in salt solutions, and in a state of dissociation at ordinary temperatures. Fresh fibrin gives off carbon dioxide, and when this is all removed by a quick stream of hydrogen, traces of it may be obtained for days by continuing the current of hydrogen. Perhaps this also is dissociation.

T. L. B.

### Causes of Variation in the Proportion of Oxygen in the Arterial System. By MATHIEU and URBAIN (Compt. rend., lxxiv, 190—194).

CHIEFLY of physiological interest. An attempt is made to show that the actions of endosmosis and of respiration respectively are antagonistic as regards the oxygenation of the blood. Diminution of temperature augments endosmosis of oxygen, whilst increased temperature decreases it. On the contrary, the respirations are increased by heat and diminished by cold.

T. S.

**On the Gases contained in the Swim-bladder of certain Fresh-water Fishes.** By F. SCHULTZE (Pflüger's Archiv. f. Physiologie, iv, 48—52).

SCHULTZE has analysed the gases contained in the swim-bladder of some fishes in a more exact manner than appears to have been done by former investigators. His analyses have been confined exclusively to fishes whose swim-bladders possess a ductus aërophorus, viz., *Cyprinus tinca* and *Barbus fluviatilis*. He finds oxygen, carbonic acid, and nitrogen in different proportions. The amount of oxygen never exceeded that of atmospheric air, and carbonic acid was always present. Carburetted hydrogen was never found. He concludes from his experiments that in such fishes the swim-bladder contains the ordinary gases found in the expiration-air of the lungs or gills, or in the intestine of the *Cobitis fossilis*.

D. F.

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**The Destiny of Peptones in the Blood.** By A. FICK (Pflüger's Archiv. f. Physiologie, iv, 40—47).

FICK gives several reasons for regarding it as probable that peptones after absorption undergo decomposition, instead of being again converted into albumin, or entering into higher combinations. Functional activity in the body generally, is associated, not so much with waste of albuminoid tissues as with combustion of non-nitrogenous material. Fick regards the non-nitrogenous products of the decomposition of the peptones as the most likely source of the combustible material used up by the muscles and other organs, and looks upon the decomposition of peptones in the liver as an important factor in the process. The great increase of nitrogenous excretion after a meal of albuminous substances cannot be accounted for in any way on the assumption that peptones enter into higher combinations, but would agree with the view that they are decomposed. Some experiments made by Goldstein, under Fick's direction, support the latter view. The experiments consisted in extirpating the kidneys of rabbits, and in comparing the normal amount of waste nitrogenous products in the blood with the amount found after solutions of peptones and albumin had been injected into the veins. The result of the few experiments made seem to support Fick's view. A greater amount of waste nitrogenous products was found in the blood after injection of peptones, and the increase observed at different periods of time after the injection corresponded with a steady process of decomposition of these substances.

D. F.

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**Alteration of the White Blood-corpuscles by Quinine.** By G. KERNER (Pflüger's Archiv. f. Physiologie, iv, 27—30).

In this paper the author brings forward additional experiments in support of his former observation, that quinine puts a stop to the motions of the white blood-corpuscles, and renders them round and darkly granulated. He also shows that this action is not due, as Stricker and



others have supposed, to the presence of free acid, as perfectly neutral hydrochloride or carbonate of quinine, in the proportion of 1 part in 4,000 of fluid, produces this effect when dissolved either in water or serum. Solutions of salicin, caffenin, atropine, and sodium arsenite, in like concentration, had either no effect or very little.

T. L. B.

**On the Presence of Hæmoglobin in the Muscles of Mollusca, and its Distribution in the Living Organism.** By E. RAY LANKESTER (Pflüger's Archiv. f. Physiologie, iv, 315—320).

THE pharynx of the *gasteropods* is red, and in *Limnæus* and *Paludina* the colour is due to hæmoglobin. This was proved by the spectroscopic appearances and changes. Perhaps as other gasteropods have their pharynges of a red colour, this is in all cases produced by hæmoglobin. The blood of the above and other gasteropods contains, however, no hæmoglobin, and is, in fact, colourless. The only molluscs in which the author has found hæmoglobin are *Planorbis* and the allied species, in which, as is well known, the blood is of a brilliant red colour. Nevertheless, although, with the above exception, no hæmoglobin can be detected in the gasteropods, it may be present in quantities too small to be detected.

The hæmoglobin is distributed through the pale yellow muscular tissue of the pharynx of *Limnæus*, and highly refractile granules are also seen. These are apparently identical with the pigment granules surrounding the ganglion cells which encompass the nerve centres, and are of a brilliant yellow or orange colour. The same granular masses are met with in the salivary glands. This yellow pigment gave no distinct absorption bands, yet the œsophageal ganglia appeared to contain hæmoglobin. It is possible that the yellow granules stand in relation to the development of the hæmoglobin in the muscular tissue, or that occasionally they may become impregnated with hæmoglobin. It is to be expected that the manner in which hæmoglobin is formed in these animals, and the form in which it exists in their muscles, will throw light upon the formation of hæmoglobin in the blood-globules of the vertebrata.

These observations are of great physiological interest, since they indicate that the province of hæmoglobin in the animal kingdom is a wide one, and is closely related to the activity of the muscular tissue. It cannot be supposed that the presence of hæmoglobin in the muscles in the above cases is a casual one. The author points out that the presence of hæmoglobin in the pharynx muscles of the gasteropods is in accordance with the observation previously made by him, that in all cases the most active and powerful muscles are furnished with hæmoglobin. In keeping with these facts also is the observation, that whilst in man the unstriped muscular fibre of the alimentary canal is free from hæmoglobin, the smooth fibres in the rectum are provided with that substance.

*Distribution of Hæmoglobin in various Organisms.*—It is asserted that hæmoglobin has been detected in the following cases by means of the spectroscope:—1. In the blood of the vertebrata the hæmoglobin is



located in the red corpuscles. In *Amphioxus* it is found in the plasma, and not in the corpuscles. 2. In most of the striped muscles of mammalia and birds; but only in the cardiac muscles, and in certain very active muscles of other vertebrata. 3. In the unstriped muscle in the human rectum. It is mostly absent in other unstriped muscles. 4. Its presence in the *Annelidæ* is variable. In some of these it is accompanied by a second dichroic substance very like hæmoglobin in its spectroscopic relations. 5. It is present in the fluid from the perivisceral cavity of the leech. 6. Hæmoglobin is distributed through the plasma of the so-called blood of the larva of *Chironomus*; but it has been sought in vain in other insects, myriapods, and arachnida. 7. It is also present in the blood-plasma of certain crustaceans, whilst in others it is absent. 8. It is, as a rule, absent from the blood of the molluscs, though it is present in the blood of a gasteropod—*Planorbis*. 9. Hæmoglobin is met with in the muscular fibres from the pharynx of gasteropod molluscs, as *Limnæus* and *Paludina*, whilst it is wanting in their blood. 10. There is perhaps some connection between hæmoglobin (which is not met with in plants) and chlorophylloid bodies.

T. S.

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**Starch in the Testicles.** By C. DARESTE (Compt. rend., lxxiv, 131).

THE author finds that the granular bodies of R. Wagner possess the optical properties of starch, and that when special precautions are taken they give the blue reaction with iodine. The starchy granules disappear during the period when spermatozoa are in the course of formation.

T. S.

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**The Physiological Properties and the Metamorphoses of Cyanates in the Organism.** By RABUTEAU and MASSUL (Compt. rend., lxxiv, 57).

THE authors find that the cyanates are destitute of toxic properties, and that these salts are converted into carbonates in the animal organism.

T. S.

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**Physiologico-Chemical Notices.** By E. SALKOWSKI (Pflüger's Archiv. f. Physiologie, iv, 91—100).

I. *On the Behaviour of some Sulpho-acids in the Organism.*—The object of the experiments related by Salkowski was to determine whether such acids as ethylsulphuric acid, sulphophenic acid, and sulphobenzolic acid have any physiological effect corresponding to the difference in their chemical constitution. Sodium-salts of these acids were administered to dogs and rabbits.

Ethylsulphuric acid in the proportion of 4—6 grams of the sodium salt seemed to produce no effect on these animals, and certainly did not cause any purgative action such as has been ascribed to its

administration. The salt apparently all passes off by the urine unchanged.

Sodium sulphophenate likewise produced no effect, and also passed off by the urine without undergoing decomposition. Free phenol was never found in the urine. These results contradict the statements of Sansom, that sodium sulphophenate is decomposed in the organism and produces the effect of phenol. The experiments of Salkowski also show that this salt has none of the antiseptic or antizymotic effect of carbolic acid.

Sulphobenzolic acid also appears all to pass off in the urine unchanged. It causes violent purging by whatever channel it is introduced into the system.

II. *A peculiar behaviour of Argento-hypoxanthin.*—Salkowski finds that when a solution of hypoxanthin, to which some gelatin has been added, is decomposed by silver nitrate, no precipitate, but only an opalescence of the liquid ensues. The opalescent liquid forms no deposit even after standing at rest for days, or on the application of heat. This property of gelatin is a point to be noticed in testing organic liquids and extracts for hypoxanthin. Neither albumin nor glycogen prevents its precipitation by silver nitrate. Gelatin appears, therefore, to act in some way independent of the mere viscosity of the liquid.

III. *Occurrence of Succinic Acid in Human and Dogs' Urine.*—Salkowski has also made some experiments with reference to the statements of Meissner and others, that in the urine of dogs, especially if fed on flesh and fat, and also in human urine, succinic acid is found in variable quantity. Salkowski criticises and points out several sources of fallacy in the method of analysis adopted by Meissner. He details several experiments of his own with reference to this point, and gives a method (for which we must refer to the original) whereby succinic acid, if added to dog's urine, can be almost entirely recovered on analysis. On analysing the urine of a dog fed for thirty days on a copious diet of flesh and fat, he did not succeed in obtaining any succinic acid. He has likewise analysed the urine of four patients, and his own urine, for several successive days, without being able to discover even the smallest trace of succinic acid.

D. F.

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**Testing of Bones for Iron.** By P. C. PLUGGE (Pflüger's Archiv. f. Physiologie, iv, 101–103).

IRON is stated by some to be a normal constituent of bone proper, while its occurrence is referred by others (Zalesky) to retained blood-colouring matter.

Plugge has taken care to avoid all conceivable sources of fallacy in his analysis. In order to separate any retained blood-colouring matter he macerated the bones in water till no residue was obtained on evaporation. He has likewise guarded against the occurrence of iron in his reagents and apparatus. From numerous analyses of different bones of different animals he comes to the conclusion that iron is

not a constituent of bone, and that if found, its occurrence is to be attributed to retained blood or impure reagents and vessels employed in analysis.

D. F.

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**Researches on Milk.** By W. FLEISCHMANN (Versuchs-Stationen Organ, xiv, 194—245).

ACCORDING to Quevenne, the casein of milk is chiefly in a state of suspension, not solution. He points out that when milk is filtered, most of the casein remains on the paper, and that the filtrate has a *lower* specific gravity than the original milk; moreover, that in asses' milk, the suspended grains of casein can be seen by the microscope; they dissolve in ammonia but not in ether. Donné and Bouchardat came to the same conclusion. According to Henle, Mitscherlich, Simon, Raspail, Mandl, A. Müller, J. Lehmann, and others, the fat-globules of milk have a thin coat of caseous or aluminous matter; while Donné, Dujardin, Guevenne, Bouchardat, and Marsiny believe that there is no coat, but that the globules are suspended as in an emulsion. The author proceeds to treat the subject mathematically. Starting from the facts that the specific gravity of butter is .942, and the diameter of the fat-globules from .01—.0016 mm., and having shown that the velocity of the globules must vary as the square root of their radius, he proves that if the serum of milk be regarded as a perfect fluid, the whole of the globules must rise as cream in 30 hours, even though they were of the smallest size known to exist, and that consequently the globules of ordinary milk should rise in far less time than this. In practice, however, only about 80 per cent. of the fat-globules rise as cream after 12 hours' standing, and the most prolonged repose does not yield more than 85—90 per cent. The globules which obstinately refuse to rise have a diameter of .0038—.0016 mm. The author concludes that the globules are impeded by adhering matter, and proceeds to calculate its quantity. Taking the specific gravity of casein as 1.486, he finds that a coat of this substance, .0000533 mm. in thickness, will suffice to prevent the globules of .0038—.0016 mm. diameter from rising, while it will allow the larger globules to do so. Further, supposing the fat to be equally distributed throughout the whole series of globules, he finds that about 20 per cent. of the fat will occur in the form of small globules which cannot rise, which is in fact the result arrived at in practice.

Numerous experiments are recorded on the rise of cream under various conditions. The quantity of cream obtained is always greater at low temperatures. Since butter contracts less by cold than the serum of milk, the velocity of the fat-globules increases with a fall of temperature, and smaller globules are enabled to rise. The volume of cream obtained is far greater at low temperatures; cream so obtained contracts on warming. The volume of the cream depends also on the size and shape of the vessel. The serum of milk becomes slightly viscid below 6°.

R. W.

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## Chemistry of Vegetable Physiology and Agriculture.

### Researches on the Nature and Origin of Ferments. By

A. BÉCHAMP (Ann. Chim. Phys. [4], xxiii, 443—453).

IN a former paper (*Compt. rend.*, lxviii, 877) the author showed that, under some circumstances, the mother of vinegar, a conglomeration of microzymes, can be transformed into bacteria, and under other circumstances into a cellular ferment which can produce the normal alcoholic fermentation from cane-sugar. The object of the present paper is to show that the converse of this is also true, and that the cellular ferment may be transformed into microzymes and bacteria.

A mixture of starch and yeast kept at a temperature of 24°—35° soon liquefies, and the yeast undergoes remarkable changes. The cells swell, become transparent, and gradually disappear. Myriads of microzymes of great agility spring into existence, then vibrios appear, and as these increase the microzymes diminish. The vibrios in their turn are succeeded by myriads of bacteria, and finally the bacteria gradually disappear, leaving nothing present but microzymes, simple or coupled together. During these changes a small quantity of gas is disengaged; no butyric acid is formed, and but little acetic and lactic acids.

A similar experiment made in presence of calcium carbonate produces somewhat similar physiological results, but, in addition, the vibrios are preceded or accompanied by a crowd of little bodies resembling the *amylobacters* of Trécul (*Compt. rend.*, lxxiii, 1453) which, however, soon disappear, leaving only bacteria present. In this experiment pure carbonic acid is disengaged at first, and afterwards a mixture of carbonic acid and hydrogen. The soluble starch and dextrin disappear, producing a corresponding quantity of alcohol, acetic, and butyric acids. The ferments which proceed from these operations can serve indifferently as lactic or butyric ferment.

As, then, the mother of vinegar when changed into bacteria becomes lactic or butyric ferment, and when transformed into cellular matter becomes alcoholic ferment, and as beer-yeast becomes lactic or butyric ferment when reduced to microzymes, vibrios, or bacteria, it is evident that the property of being a ferment of any particular nature does not depend essentially upon the matter of the ferment, but upon its organization or structure.

J. B.

### Origin of Lactic and Alcoholic Ferments. By A. TRÉCUL (*Compt. rend.*, lxxiii, 1453—1461).

THIS paper discusses the germ theory of Pasteur, and the author states that spontaneous fermentation is not due to inoculation by germs, but to changes produced in the albuminoid matter in solution. Under favourable circumstances the following series of transformations takes place in a malt wort:—The albuminoid matter produces bacteria (or

passes directly into alcoholic ferment, or into *mycoderma*); the bacteria then change successively into lactic ferment, alcoholic ferment, *Myco-derma cerevisia*, and finally into *Penicillium*.

J. B.

**Development of Alcoholic and other Ferments in Fermentable Mixtures, without the Direct Intervention of Albuminoid Substances.** By F. BÉCHAMP (Compt. rend., lxxiv, 115—119).

LIEBIG contests the statement that an alcoholic ferment can be produced in a saccharine mixture without the previous addition of an albuminoid substance; yet nothing is more certain. A mixture of 250 grams of cane-sugar, 1 gram of magnesium phosphate, 0.5 gram of calcium phosphate, and 1500 cc. of water, when exposed to the air, soon became very acid; gas was given off as abundantly as in a fermentation with ordinary yeast; and in 91 days, when the evolution of gas had ceased, the mixture yielded 356 cc. alcohol of 36 degrees. Acetic acid was also present, but neither butyric nor lactic acid. The ferment consisted of very small oval cells and mobile granulations. Experiments with cane-sugar and other salts, as potassium nitrate, sodium phosphate, alum, &c., gave very similar results.

J. B.

**On the Cause of Alcoholic Fermentation by Beer Yeast, and on the Formation of Leucine and Tyrosine in that Fermentation.** By A. BÉCHAMP (Compt. rend., lxxiv, 184—188).

THE first part of this paper is devoted to the views of Liebig upon this subject. In a former note (Compt. rend., lxi, 689) the author showed that beer yeast, when suspended in water, exhausts itself and secretes phosphoric acid, and that amongst other products formed, one, named by him *zymase*, is capable of inverting cane-sugar. In the present paper it is stated that the phosphoric acid and *zymase* exist in the interior of the yeast-cells, from which they are separated by exosmose, and that amongst the other products are leucine and tyrosine. An experiment upon 350 grams of moist yeast, representing 84 grams of the dry substance, furnished 5 grams of leucine and 5 decigrams of tyrosine.

J. B.

**On Cells of Yeast becoming Mobile, like Monads.** By A. TRÉCUL (Compt. rend., lxxiv, 23).

WHEN the yeast which works off from new beer in cask during the process of cleansing is allowed to settle, the fluid portion removed, and water added to the remainder, nearly all the cells of yeast rise to the surface in three days, and under the microscope they are seen to move with the agility of the most active monads. These bodies resemble in size and shape the yeast-cells from which they have been derived, and their surface is covered with fine dark granules which appear to have resulted from an alteration of the superficial membrane.

J. B.

**Note on the Pretended Transformations of Bacteria and Mucedinea into Alcoholic Ferments.** By J. C. DE SEYNES (Compt. rend., lxxiv, 113).

THE author has devoted attention for some years to bacteria, ferments, mucedinea, penicillium, and other mucedinea, without ever having witnessed the transformations announced by Hallier, and partly admitted by Trécul. When penicillium is caused to vegetate in water, the plasma after some time undergoes notable changes, and divides into very distinct granulations, but these granulations have never been observed to pass into the state of bacteria.

J. B.

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*On the Nature of Fermentation and the Origin of Ferments:* see further,—FRÉMY (Compt. rend., lxxiv, 164, 270, 355); BALARD (*ibid.* 162, 289, 366); BLANCHARD (*ibid.* 167); WURTZ (*ibid.* 292); DUMAS (*ibid.* 366); TRÉCUL (*ibid.* 153); RHEINECK (*Dingl. polyt. J.*, ccii, 282); W. H. WOOD (*Chem. News*, xxiv, 246).

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**Influence of various Colours on Vegetation.** By P. BERT (Compt. rend., lxxiii, 1444—1447).

THE author has grown various plants and seeds under the influence of different coloured lights. Care was taken to have the plants in the same condition as far as possible. Plants of various classes were experimented on, such as those which flourish in strong sunlight, those which flourish in the shade, succulent plants, &c. They were exposed beneath frames with different coloured glasses, seven of these were used in all: 1 a frame with ordinary glass, 2 with ground glass, 3 with blackened glass, 4 with red glass, 5 with yellow glass, 6 with green glass, and 7 with blue glass. The light transmitted through each of these glasses was nearly monochromatic. The author draws from his experiments the following general conclusions:—

1. That green light is almost as fatal to vegetation as darkness.
2. That red light is very detrimental to plants, though in a less degree than the green light employed.
3. That though yellow light is far less detrimental than the preceding, it is more injurious than blue light.
4. That all the colours taken singly are injurious to plants, and that their union in the proportion to form white light is necessary for healthy growth.

The author has examined the transmitted light from the leaves of various plants, and finds that there is a slight difference in the rays which different leaves absorb and utilize; this, he believes, explains the fact that certain plants flourish in the shade of trees, whilst others will scarcely exist; in the former case it is supposed that the rays required by the plant are not absorbed by the leaves of the trees, but in the latter they are.

A. P.



**Decoloration of Flowers by Electricity.** By M. BECQUEREL  
(Third Memoir. Compt. rend., lxxiii, 1345—1347).

IN two former communications the author has described the decolorizing effects of feeble currents of electricity, and of high and low temperatures, on the flowers and leaves of plants. From further experiments he concludes that these effects are mostly due to a mechanical destruction or alteration of the envelopes of the cells containing the colouring matters; these colouring matters escaping to the exterior react on the surrounding liquids, the result of which is a change of the colours, ending in their complete destruction. The author believes the fading of flowers to be due to the same action produced by solar heat. It is probable that similar effects are produced in the fine tissues of animal organization; the beneficial application of electricity to therapeutics may be due to the destruction of false membranes, slight deposits, the cause or effect of disease, which are more easily decomposed than healthy tissue, and on the destruction of which the disease disappears. The brilliant colours of the wings of butterflies, as well as of certain birds, are not affected by electrical discharges; their colours are either due to an insoluble matter contained in their cells, or perhaps to the interference of light.

A. P.

**Quantity and Composition of the Stubble and Roots remaining in the Field after Harvest.** By H. WEISKE (Versuchs-Stationen Organ, xiv, 105—118).

THE portion of a crop left on the field as stubble and roots has been seldom examined; it is clearly of importance, as furnishing by its decomposition available food for the succeeding crop. In these experiments the roots were collected from the first ten inches of soil; the roots in the subsoil are therefore not included. The quantities of the principal constituents found in the residues of various crops are given below in pounds per English acre.

Crop.	Total dry substance.	Organic substance.	Ash.	Nitrogen.	Lime.	Magnesia.	Potash.	Soda.	Suburic acid.	Phosphoric acid.
Lucerne .....	9702	8498	1204	137	197	25	37	27	19	40
Red clover .....	8953	7026	1927	193	263	50	82	20	26	75
Sainfoin .....	5952	4925	1027	124	118	32	43	14	21	30
Kidney vetch .....	5023	4044	979	103	137	18	26	6	14	24
Serradilla .....	3141	2594	547	65	80	14	9	5	9	19
Lupine .....	3547	2994	553	63	81	12	17	4	7	14
Peas .....	3234	2560	674	57	72	11	11	7	10	15
Buckwheat .....	2203	1736	467	48	81	7	9	4	7	11
Rye .....	5283	3630	1653	66	74	15	32	43	12	26
Wheat .....	3490	2396	1094	24	77	10	19	11	8	12
Oats .....	3792	2343	1449	27	86	12	25	18	9	30
Barley .....	1999	1617	382	23	43	6	10	4	6	12
Rape .....	4475	3850	625	61	124	13	47	21	31	32

The amount of ash is in all cases high, probably from the difficulty of entirely separating adhering earth. The ash contained 45—84 per cent. of sand and silica, the proportion of these being highest in the case of rye, oats, and wheat. The immense residue of nitrogen, and other elements of plant-food, left by red clover and its allies, is perhaps the most important feature of the results.

R. W.

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**Ash Analysis of the Seed of *Hyoscyamus Niger*.** By  
E. REICHARDT (Versuchs-Stationen Organ, xiv, 149—150).

THE dry seed yielded 2.43 per cent. of ash. In the analysis of the ash the alkalis and chlorine were determined from seed which had been merely charred. The composition of the ash was found to be as follows:—

K <sub>2</sub> O.	Na <sub>2</sub> O.	CaO.	MgO.	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	Cl.	CO <sub>2</sub> .	SiO <sub>2</sub> .	Sand.
17.54	5.40	6.02	19.98	1.92	0.63	42.45	0.73	0.30	0.15	0.68	3.20=99.00

The large proportion of magnesia and phosphoric acid is remarkable.

R. W.

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**Analytical Chemistry.**

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**On a New and very Delicate Test for Ammonia.** By  
R. BÖTTGER (N. Repert. Pharm., xxi, 50).

WHEN to a solution containing the smallest quantity of ammonia, or of an ammoniacal salt, a few drops of a watery solution of carbolic acid are added, and then a little filtered solution of chloride of lime, the liquid becomes green, especially on warming.

The so-called ozone-water of commerce was found to contain no ozone, but a trace of nitrous acid.

C. H. G.

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**On the Estimation of Lime.** By AUG. SOUCHAY; and Notes  
on the Foregoing. By R. FRESSENIUS (Fresenius Zeitschrift, 323—329).

THE authors have deduced from their experiments the following facts regarding lime estimations:—

1. That in such estimations the lime should not be weighed as CaO, because in heating the precipitated calcium oxalate it is very difficult perfectly to drive off every trace of carbonic acid, and so the results are generally too high.

2. That the transformation of the calcium oxalate into carbonate by gentle warming, treating with ammonium carbonate, and again heating, gives the most correct and concordant results.

M. M. P. M.

**On the Estimation of Calcium Sulphide in Bone Char.** By C. FAHLBERG (*Fresenius Zeitschrift*, 329—332).

THE author employs a modified form of Scheibler's apparatus for estimating carbonic acid in char. The sulphuretted hydrogen evolved by the action of acid on the char, he condenses in a U-tube, by means of pumice stone soaked in a solution of copper sulphate.

The results obtained are harmonious, differing not more than, at the most, .014 per cent.

M. M. P. M.

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**On the Influence of an Ammonium Salt in the Precipitation of Phosphoric Acid by Ammonium Molybdate.** By J. KÖNIG (*Zeitschrift für Anal. Chem.*, x, 305).

THE author recommends the process of Fresenius, Neubauer, and Luck, for estimating the so-called reduced phosphates. He shows that by the action of ammonium oxalate and citrate, not only is the phosphoric acid of tricalcium phosphate brought into a soluble form, but also that precipitated iron and aluminium phosphates are made soluble; from these solutions, however, the phosphoric is not at all, or only partially, precipitated by ammonium molybdate in presence of nitric acid. Even if the phosphate be dissolved in nitric acid, and ammonium oxalate added, this non-precipitation ensues.

Of the various ammonium salts which prevent the precipitation of phosphoric acid by ammonium molybdate, the citrate and oxalate are the most energetic in their action.

M. M. P. M.

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**Note on Fresenius' Process for the Recovery of Molybdic Acid from Residues.** By F. MUCK (*Zeitschrift für Anal. Chem.*, x, 307).

THE author objects to Fresenius' method for the recovery of molybdic acid (p. 1092 of last volume), that it involves the evaporation of large solutions, the addition of ammonium salts, and the treatment of the residue after evaporation with ammonia, this last operation being often very troublesome, owing to the presence of iron and calcium salts.

A process for the recovery of molybdic acid from these residues was given by the author two years ago (*Zeitschr. Anal. Chem.*, viii, 377).

M. M. P. M.

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**On Manganese Analysis by the Method of Fresenius and Will.** By E. LUCK (*Zeitschrift für Anal. Chem.*, x, 310—322).

THE author has investigated the effect exercised by small quantities of metallic iron, or ferrous salts, which may be mixed with manganese oxide when the manganese is estimated by the above method. His results show—



1. The presence of iron or ferrous salts causes a lower result to be obtained than when these substances are absent; but even the amount of manganese thus obtained is higher than what would actually be found by such a method as that of Bunsen.

2. If the evolution of carbonic acid be rapid, then some of this gas escapes not perfectly dry, and consequently the results obtained are too high; in presence of iron protoxide sometimes as much as 2 per cent. to 3 per cent. more  $\text{MnO}_2$  is obtained when the process is rapidly, than when it is slowly, carried on.

3. If 6—8 cub. cent. of sodium acetate solution (1.9) be added, all the ferrous toxide is oxidised, and the process, whether slowly or quickly carried on, gives results practically identical with those obtained by Bunsen's method.

4. The temperature should never exceed  $70^\circ \text{C.}$ , or the oxalic acid is liable to be decomposed into carbon mono- and di-oxides; nor (for a similar reason) should the process be carried on in direct sunlight.

M. M. P. M.

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**Analysis of the Gases of the Blood.** By ESTOR and SAINT-PIERRE (Compt. rend., lxxiv., 257, 330).

THE authors at first employed the method of Cl. Bernard, *i.e.*, displacing the gases of the blood by carbonic oxide. To avoid transfers they also used a curved collection tube with two branches. In another experiment the blood and carbonic oxide were introduced into a tubulated collection-tube with a mercury pump attached; this method much facilitates manipulation. A third process extracts the gas simply by a vacuum, without carbonic oxide, the vacuum being given by a barometer with an enlarged chamber communicating with the mercury pump. All these methods yield the same results with the same sample of blood. The authors have already published plates and details.

The blood of the dog gives the following average quantities of oxygen per 100 c.c.:—Renal artery, 18.22 c.c.; splenic, 14.38 c.c.; crural, 7.62 c.c., whichever of the three modes of analysis may be adopted. Some German observers having however obtained very different numbers by Ludwig's process, the authors remark that that process involves admixture of the blood with water. They have further discovered that, though cold water effects no change in the results, hot water and boiling increase the average quantity of oxygen from the crural artery to 19 c.c. per 100 of blood.

C. G. S.

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**Detection of Spirit in Essential Oils.** By H. HAGER (Chem. Centr., 1871, 821).

THE author shows that oils which have become somewhat oxidised are capable of dissolving a certain quantity of fuchsine, even if they contain no alcohol, and that the use of fuchsine, as recommended by Pascher, is inadmissible for oils which are of such a colour as to mask that of

the test body, even if it goes into solution. The author insists on the superior advantages of his own test of adding to the oil a bit of solid tannin, which becomes moist and slimy if any spirit be present.

C. H. G.

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**Testing Crude Carbohc Acid.** By Dr. G. LEUBE, Jun. (Dingl. polyt., ccii, 308).

WEIGH off 5 grm. of the sample and shake with 100 grm. of water, allow tar, &c., to settle, draw off 10 cc. of the clear solution, to which add 10 drops of a solution containing 1 part of ferric chloride in 9 parts of water. Compare the colour so produced with that of a number of solutions freshly prepared by adding a like quantity of iron solution to solutions of pure carbohc acid containing 0.25, 0.20, 0.15 grm. to 100 cc., &c.

C. H. G.

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**Simplified Method of Estimating Carbonic Acid in the Saturating Gas of Sugar Factories.** By Dr. C. STAMMER (Dingl. polyt. J., ccii, 368).

A ROUGH method for every day use by non-chemists, which would not probably give results nearer than 1 per cent. on total volume of gas employed.

C. H. G.

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*On the Loss of Weight of Platinum Crucibles in a Gas Flame.* By F. STOLBA (N. Repert. Pharm. xxi, 52).

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## Technical Chemistry.

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**Inconveniences presented by the Substitution of Soda for Potash.** By P. CARLES (J. Pharm. [4], xiv, 413—415).

THE following examples are given of the inconveniences resulting from the substitution of soda for potash.

In the preparation of potassic iodide, if the potash employed contains soda, there is a notable loss of iodine during the calcination; the product is alkaline from the presence of sodic carbonate, and the sodic iodide renders the salt deliquescent. The same results are not met with in making the bromide.

Potash mixed with soda is inappropriate for the absorption of carbon dioxide in Liebig's bulbs; for the sodic carbonate formed renders the solution turbid, and impedes the passage of the gas.

Polysulphide of potassium is now generally replaced by the corresponding sodium compound. It is more active: for on account of the lower equivalent of sodium, the sodic salt contains a greater percentage of the active ingredient of the compound, viz., sulphur. The caustic

made from impure potassic hydrate is also rendered less useful in medicine by the presence of soda.

Lastly, sodic silicate cannot replace potassic silicate in lutes, on account of the non-drying property of the former.

T. S.

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**Note on the Detonating mixture of Potassium Nitrate and Sodium Acetate.** By H. VIOLETTE (*Ann. Chim. Phys.* [4], xxiii, 306—310).

A LABORATORY accident in the first instance, brought the following unexpected reaction before the author's notice.

If a mixture of equal parts of potassium nitrate and sodium acetate be fused in a platinum capsule, and the temperature carefully maintained at or about  $300^{\circ}$ , the melted salt remains liquid without sensible alteration; but if the heat be raised to  $350^{\circ}$ , a slight ebullition takes place, which is immediately followed by a violent explosion, attended by a flash and loud report, in every respect similar to the detonation which takes place when gunpowder is fired. Nothing remains in the capsule, save a very small residue, consisting of alkaline carbonate.

If, while the salts are maintained in tranquil fusion at a temperature about  $300^{\circ}$ , an ignited splinter be plunged into the liquid, the explosion is instantly determined.

In preparing the above mixture, if the nitrate is used in excess, deflagration does not take place; if the acetate predominates, the mixture takes fire, but the combustion is incomplete; the addition of a tenth part of sulphur, however, renders the explosion more luminous and more violent. A mixture of potassium nitrate with other acetates (those of copper, barium, for example) does not produce an explosive compound.

The author has undertaken numerous experiments with the view of ascertaining the value of the foregoing mixture as an explosive agent, but at present they do not appear to have led to any practical results. He admits that the mixture is very hygroscopic, and that if prepared by triturating the dry salts together, as in the preparation of gunpowder, it is apt to burn slowly, and with an uncertain action.

J. W.

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**Suggestion for the prevention of Explosions in working with Fulminating Mercury and other Inflaming Compositions.**  
By PH. NEUMANN (*Dingl. polyt. J.*, ccii, 271—275).

THE author suggests that a mixture of cupric cyanide and potassium chlorate might be employed as a comparatively safe substitute for mercuric fulminate mixtures, and that the danger incurred in preparing the latter might be diminished by performing the manufacturing operations in a rarefied atmosphere.

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**On the Yellow and Red Arsenic Pigments.** By MAX  
BUCHNER (*Zeitschrift für Anal. Chem.*, x, 308).

As the composition of these pigments has never been clearly settled, the author has performed a number of analyses of various samples, from which he concludes that yellow arsenic, as used for a pigment, contains from 93 to 97 per cent. of arsenious acid, while the red pigment contains generally all its arsenic as arsenic disulphide, together with an excess of free sulphur. The former substance is thus extremely poisonous, being indeed nearly as much so as the ordinary white arsenic.

M. M. P. M.

**Hydraulic Properties of Ignited Gypsum.** By FREDERICK  
SCHOTT (*Dingl. polyt.*, ccii, 355—364).

THE previous experiments of the author on Scott's cement showed that the proportion of lime to gypsum might be greatly varied without the ignited mass losing its hydraulic properties. The present experiments are directed to show whether the lime may not be entirely omitted, *i. e.*, whether the hydraulic properties of the cement do not reside in the altered gypsum alone. They show that ordinary plaster of Paris, or crystallised selenite, or anhydrite, when heated to a temperature between 400° and 500° C. or higher, ceases to behave like ordinary "plaster," but acquires true hydraulic properties, and sets after a greater or less time (three days to three weeks) into a white mass having an alabaster-like semi-transparency. The addition of lime is, however, useful as giving the cement a greater density and consequent hardness.

C. H. G.

**On Superphosphate.** By R. JONES (*Versuchs-Stationen Organ.*, xiv, 77—105).

STROHMEYER and Crum have stated that  $1\frac{1}{2}$  equivalent of sulphuric acid is sufficient for the solution of 1 equivalent of tricalcic phosphate. Piccard and the author have shown that 2 equivalents of acid are required. With two equivalents of very dilute acid Piccard dissolved, as a maximum,  $\frac{1}{4}\frac{4}{5}$  equiv., and the author  $1\frac{5}{8}\frac{4}{5}$  equiv. of tricalcic phosphate. When the digestion of the materials was prolonged beyond an hour or two, a smaller fraction was found in solution.

Piccard states that when less than 2 equivs. of acid are employed, a proportionate amount of phosphate is in the first instance dissolved; but on standing, the excess of tricalcic phosphate reacts upon the soluble acid phosphate, and the quantity of the latter is diminished. When superphosphates made with pure materials are dried, the author finds that the amount of soluble phosphate becomes less; the diminution is in proportion to the extent of dessication, and is much greater when the acid employed has been deficient. Superphosphates thus injured increase in soluble phosphate if they absorb moisture; and when they are treated with water, the amount of phosphoric acid dissolved con-

tinues to increase by long digestion in the cold. Experiments on these phenomena led to the following conclusions: When 2 equivalents, or less, of moderately dilute sulphuric acid act upon tricalcic phosphate, monocalcic phosphate, but no free phosphoric acid, is apparently at first produced. During drying, a portion of the monocalcic phosphate disappears, and phosphoric acid and basic phosphates are formed, which latter, according to circumstances, are composed of  $\text{Ca}_5\text{H}_{14}\text{P}_8\text{O}_{32}$ ,  $\text{Ca}_3\text{H}_6\text{P}_4\text{O}_{16}$ , or  $\text{CaH}_4\text{P}_2\text{O}_8$ . On again absorbing water, these phosphates revert, more or less completely, into phosphoric acid, and monocalcic and tricalcic phosphates. The author examined many commercial superphosphates; he shows that the insoluble phosphates generally contain much more phosphoric acid than belongs to tricalcic phosphate. Free phosphoric acid is usually present in superphosphates; it may be determined by exhaustion with alcohol. Free sulphuric acid seldom occurs; it is not found in the alcoholic extract, as it at once reacts on any insoluble phosphate present. The author detects it by treating the superphosphate with a little water, and quickly filtering; the formation of a crystalline precipitate of gypsum on standing indicates free sulphuric acid. It follows from the author's experiments, that the sulphuric acid employed for the manufacture of superphosphate will never yield the theoretical amount of soluble phosphate.

R. W.

### On the Solubility of some Forms of Calcic Phosphate. By CHARLES P. WILLIAMS (Chem. News, xxiv, 306).

THE solubility of tricalcic phosphate in water saturated with carbonic acid depends in great measure upon the source from which it has been derived. Thus Bischoff has shown that, while one part of apatite will dissolve in 393,000 parts of water saturated with carbonic acid, the artificially prepared basic phosphate requires only 1102 parts of the same for its solution; and since theoretical considerations would appear to indicate that all forms of calcium phosphate must pass to a condition resembling that of the artificially precipitated phosphate before they are capable of being assimilated by vegetation, the rapidity of the action of carbonic acid water in rendering phosphates soluble becomes a measurable indication of the relative rapidity of their action when applied as fertilisers.

The writer has endeavoured to determine the solubility of some of the best known forms of natural tricalcic phosphate by operating in the following manner:—

A weighed quantity of the finely powdered material was placed in one litre of water, and carbonic anhydride passed through the same for fifty hours at a temperature of  $15.5^\circ$ . At the expiration of this time the liquid was filtered off; the filtrate, after the addition of nitric acid, concentrated by evaporation, and the phosphoric acid separated by the addition of ammonium molybdate. The precipitate thus obtained was converted into ammonio-magnesium phosphate, and the phosphoric acid calculated in the usual manner. Great care was taken to conduct the experiments with uniformity, and the amount of material operated

upon was made to correspond with the percentage of real phosphoric acid present, the latter having been previously determined by analysis.

*Experiment 1.*—Apatite from Perth, Canada, containing 89.27 per cent.  $\text{Ca}_3\text{P}_2\text{O}_8$ . Solution contained 0.0021 gram  $\text{P}_2\text{O}_5$ , equivalent to 0.0045  $\text{Ca}_3\text{P}_2\text{O}_8$ . One part of the apatite dissolved in 222,222 parts of water saturated with carbonic acid.

*Experiment 2.*—Same as in No. 1, but the material levigated. One part was found to dissolve in 140,840 parts of water saturated as before.

*Experiment 3.*—Finely ground bone, containing 56.78 per cent. phosphate. One part dissolved in 5698 parts of water saturated with carbonic acid.

*Experiment 4.*—To ascertain whether the organic matter of the bone exercised any influence upon its solubility, a portion of the material used in No. 3 was carefully calcined. One part was then found to require 8029 parts of water for its solution.

*Experiment 5.*—South Carolina phosphate, containing 57.89 per cent. of  $\text{Ca}_3\text{P}_2\text{O}_8$ . One part dissolved in 6983 parts of water saturated with carbonic acid.

*Experiment 6.*—Phosphatic guano from Orchilla Island, containing 49.67 per cent. phosphate. One part dissolved in 8009 parts of water saturated with carbonic acid.

These experiments rather enhance than decrease the difficulties of discriminating between the chemically precipitated and the originally undecomposed phosphate contained in an artificial manure; but they afford additional evidence of the value of this precipitated or "returned" phosphate, by showing how much more rapid it is in action than any other variety of phosphate, no matter to what degree of fineness the latter may be brought by purely mechanical means of subdivision.

J. W.

### Iron-minium. (Chem. Centr., 1871, 815.)

A RICH iron ore, in small pieces (Stuferze), is roasted strongly, so as to thoroughly expel the water of hydration, then powdered in stamping mills, and carefully levigated. The finest portions are separately dried and finely mealed between rollers. The material so obtained is used as a substitute for red lead as a cement and as a pigment.

C. H. G.

### Behaviour of Dialysed Oxide of Iron. By J. ATHENSTADT (Chem. Centr., 1871, 822).

THE addition of a weak solution of a fixed organic acid, of an alkali, or of salts, causes the formation of a clear jelly, completely and easily soluble in distilled water. If the solutions are too concentrated the jelly is cloudy and insoluble.

C. H. G.



**Acetate of Silver from a Photographic Silver-Bath.** By A. VOGEL (N. Repert. Pharm., xxi, 6).

BATHS alternately acidulated with acetic acid and neutralised by ammonia, naturally deposit some of this slightly soluble salt.

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**Organic Matter in Building-Rubbish.** By A. VOGEL (N. Repert. Pharm., xxi, 8).

THE finer portions, sifted from stones, &c., of the rubbish from the walls of an old dwelling house, were found to contain matter insoluble in acid 22·6 per cent., calcic carbonate 75·75 per cent., iron oxide 1·5 per cent. Heated in a glass tube it turned brown, and gave off ammonia, and when ignited with soda-lime gave 0·1 to 1·16 per cent. of nitrogen. When repeatedly moistened with water and exposed to the air it became covered with mould, and gave off an unpleasant smell.

C. H. G.

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**A New Process for Preparing fully developed Crystals.** By F. SCHULZE (N. Repert. Pharm., xxi, 53).

THE process consists in applying a gelatinising solution (of apiin, pectin or gelatin) as a solvent of the salt to be deposited on a crystal suspended in the jelly.

C. H. G.

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**Solvents for Indigo.** (Dingl. polyt. J., ccii, 307.)

IN addition to the solvents aniline, petroleum, &c., there are named nitrobenzene (as good as aniline), castor-oil, acetone, chloral hydrate, camphor, copaiba balsam, amyl alcohol, lavender oil, white beeswax, Japanese vegetable wax, and Carnauba wax.

C. H. G.

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**Preparation of Safranine.** (Dingl. polyt. J., ccii, 307.)

TWO parts aniline nitrite are heated for five minutes with one part arsenic acid to a temperature of 80°—120° C., the mixture poured into boiling water, and neutralised with lime. The solution, now of a fine red colour, is allowed to stand a short time, filtered through woollen bags, and treated with common salt to precipitate the yellow colouring matter, which only requires to be collected and drained in order to be fit for use.

The nitrite of aniline is prepared by passing nitrous acid, prepared from starch and nitric acid, into aniline, and washing the product two or three times.

C. H. G.

**To protect Thickening from turning Sour and Mouldy.**  
(Dingl. polyt. J., ccii, 308.)

CAUSTIC soda saturated with crude carbolic acid is as effective as zinc chloride, and does not rot the fibre of the goods.

C. H. G.

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**Preservation of Hops.** (Dingl. polyt. J., ccii, 309.)

HOPS buried in ice for seven months ending in September, were found to possess all the qualities of young new hops.

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**Preserving Paper Labels on Glasses** (Ibid., 312).

THE dry label is rubbed with a piece of paraffin and smoothed with a glass rod.

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**On Softening Water with Lime.** By JOHN STINGL (Dingl. polyt. J., ccii, 364—368).

THE paper contains full analyses of a given water before and after treatment by Clarke's process; also of the deposit formed by the precipitation, and of the boiler incrustation given by the treated and untreated water. To give any further idea of the paper it would be necessary to reprint the numerous tables of analysis.

C. H. G.

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*Application of Tannin to the Treatment of Wines.* (Dingl. polyt. J., ccii, 310).

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*Removal of Yeast from Wine Casks* (Ibid., 311).

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*Detection of the Adulteration of Wine with Fruit Wines* (Ibid., 312).

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*Preparation of Collodion.* By A. VOGEL (N. Repert. Pharm., xxi, 6).

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*New Process for Determining the Igniting Points of Petroleum Oils.*  
By DR. VAN DE WEYDE (Scientific American, 1871, 162; Dingl. polyt. J., ccii, 301).

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## PAPERS READ BEFORE THE CHEMICAL SOCIETY.

IX.—*Note on the Quantity of Cæsium contained in the Water of the Hot Spring found in Wheal Clifford.*

By COLONEL PHILIP YORKE, F.R.S.

At the meeting of the British Association, held at Bath, in 1864, the President, Sir Charles Lyell, gave an account in his address of this hot spring, found in the 220 fathom level of the above-mentioned mine; and an analysis of the water by Dr. W. A. Miller, appeared in the transactions of the chemical section for the same year.

The temperature of the spring was  $125^{\circ}$  F. The analysis showed the water to contain 646 grains of saline matter in the gallon. The preponderating substance was common salt, but the most remarkable was chloride of lithium, of which the gallon contained 26 grains. Dr. Miller also states that the water contained chloride of potassium, with a little chloride of cæsium.

In 1866 I visited Wheal Clifford, and at my request the superintendent of the mine was kind enough to undertake to boil down 80 gallons of the water to 2 gallons, and this quantity was forwarded to me in London.

The specific gravity of this liquid was  $= 1.210$ , and the total quantity of saline matter contained in it was about one-sixth less than that indicated by Dr. Miller's analysis.

To ascertain the quantity of cæsium, 5 pints of the concentrated water ( $= 25$  gallons of the spring water) was experimented on. The earthy bases, the lithium chloride, and the greater part of the sodium chloride, were separated, and to the solution of alkaline chlorides remaining, solution of platinic chloride was added. The precipitate was washed with small quantities of hot water, until the washings were very slightly coloured. The precipitate, which was of a pale yellow colour, was then dried: it weighed 7.5 grs. Before the spectroscope this substance gave the blue lines of cæsium very distinctly, and I did not observe any potassium lines.

The greater part of this precipitate was placed in a U-shaped tube, and heated to  $105^{\circ}$  C., until the weight was constant and  $= 5.925$  grains. The tube was then heated by a spirit lamp to a temperature below visible redness in daylight, while a current of dry hydrogen was passed through it.

The loss amounted to 1.315 grains. Water was added to the black



residue in the U-tube, which was washed, the liquid was evaporated in a platinum crucible, and the residue gently ignited: it weighed 2·713 grains. The platinum dried and heated weighed 1·84 grains.

We have then:—

Loss.....	=	1·315	} = 5·87
Chlorides ignited .....	=	2·715	
Platinum.....	=	1·84	

If the chloroplatinate of cæsium be represented by  $\text{CsCl} = 168\cdot5$  }  
 $2\text{Cl} = 71$  }  
 $\text{Pt} = 99$  }

then 100 parts should consist of  $\left\{ \begin{array}{l} \text{CsCl} = 49\cdot78 \\ 2\text{Cl} = 20\cdot97; \text{ found } \left\{ \begin{array}{l} 46\cdot25 \\ 22\cdot403. \\ 31\cdot345 \end{array} \right. \\ \text{Pt} = 29\cdot23 \end{array} \right.$

If the 46·25 chlorides be assumed to be a mixture of the chlorides of cæsium and potassium, and the quantities of each be calculated from

the quantity of platinum, 100 parts would consist of  $\left\{ \begin{array}{l} \text{KCl} = 5\cdot60 \\ \text{CsCl} = 40\cdot65 \\ 2\text{Cl} = 22\cdot40' \\ \text{Pt} = 31\cdot32 \end{array} \right.$

7·5 grains chloroplatinate would therefore contain 3 grains of cæsium, and this would be the quantity yielded by 25 gallons, or about 250 lbs., and a million parts of the water would contain 1·71 CsCl, or a gallon 0·12 grains.

The Dürkheim water, according to Bunsen, contains 0·17 CsCl in a million parts.

I think, then, that we are entitled to infer from the experiment related, that the Wheal Clifford contains at least 10 times as much chloride of cæsium as that of Dürkheim, but probably a larger proportion.

#### X.—On Meta-stannic Acid, and the Detection and Estimation of Tin.

By ALFRED H. ALLEN.

RECENT experiments led me to examine the characters of meta-stannic acid, when I obtained some results which were greatly at variance with the properties hitherto ascribed to it.

I prepared a quantity of meta-stannic acid by acting on granulated tin with nitric acid, evaporating nearly to dryness, diluting, and washing well by decantation and on the filter. Portions of the product were boiled with concentrated hydrochloric acid (sp. gr. 1·11) in moderate quantity for a few minutes, the residue allowed to settle, and

the clear liquid was decanted and tested with hydrosulphuric acid. The liquid in every case contained abundance of tin; and when much hydrochloric acid was employed the solution was sometimes nearly perfect. The residue possessed the properties attributed to it by Miller and Fresenius, but its aqueous solution showed far less liability to precipitation by excess of acid than I had expected. Any method of analysis depending on the insolubility of meta-stannic acid in hydrochloric acid is utterly worthless.\* The presence of stannic phosphate or arseniate in no way alters the solubility of meta-stannic acid, but renders the solution liable to precipitate on addition of water, especially when heated.

The residue left when antimony has been oxidised by nitric acid is perfectly soluble in hydrochloric acid.

When meta-stannic acid is heated to boiling with strong sulphuric acid, it dissolves completely, becoming converted into ordinary stannic sulphate. If the liquid be poured into cold water, a solution of stannic sulphate is at first obtained, but this quickly deposits some of the tin as *ortho*-stannic hydrate, the precipitate giving no yellow stannous meta-stannate when moistened with stannous chloride. On boiling the solution of stannic sulphate, the whole of the tin is precipitated as *meta*-stannic acid.

There is thus a close analogy in the behaviour of stannic and titanous sulphates, when treated with water, though the latter compound does not seem to be decomposed by mere dilution, but is completely decomposed by long-continued boiling.

Commercial stannic oxide (freed from lead by nitric acid) when heated with concentrated sulphuric acid is partially converted into stannic sulphate, but I have not succeeded in obtaining complete solution.

When meta-stannic acid is fused with hydro-potassic or hydro-sodic sulphate, a product is obtained which dissolves partially in cold water, the solution containing a small quantity of tin, as stannic sulphate; meta-stannic acid is precipitated from it by boiling.

The portion insoluble in cold water also contains stannic hydrate, which, by treatment with boiling water, forms meta-stannic hydrate. It is completely and readily soluble in hydrochloric acid.

Ignited stannic oxide is also acted on by hydro-potassic sulphate, and the product contains stannic hydrate, which is entirely precipitated by boiling. In this respect, therefore, tin shows its usual resemblance to titanium. The fused product is readily soluble in hot hydrochloric acid, but a second fusion is sometimes necessary to effect perfect solution.

\* Fresenius makes use of the supposed insolubility of meta-stannic acid in hot concentrated hydrochloric acid in his method of qualitative analysis. (7th edition, page 110.)

Native stannic oxide (crystallised cassiterite) when finely powdered, is largely converted into a soluble modification by fusion with hydropotassic sulphate, but I did not succeed in effecting complete decomposition, even by a second fusion. For the estimation of the tin I prefer to fuse with potassium cyanide.

On adding about twice the bulk of strong hydrochloric acid to the stannic sulphate, a solution is formed which will bear copious dilution without suffering precipitation. This solution gives *no* yellow colour with stannous chloride, as would be the case were *meta*-stannic chloride present. On addition of tartaric acid and excess of ammonia, a perfectly clear solution is obtained, from which any phosphate or arseniate can be directly precipitated as the ammonio-magnesium salt. (Meta-stannic acid is not dissolved by addition of tartaric acid and excess of ammonia.) If ammonia be added to the solution, the precipitate produced is readily soluble in nitric acid, and the solution so obtained can even be boiled without precipitation. Of course, were meta-stannic acid present, no solution could be effected by nitric acid.

These results all prove that hot concentrated sulphuric acid converts meta-stannic acid into ortho-stannic sulphate, a change similar to that produced by prolonged treatment with hot hydrochloric acid, which is stated by Watts to convert it into normal stannic chloride.

The residue left by the oxidation of *antimony* by nitric acid is readily acted on by strong sulphuric acid, but the solution produced by subsequent treatment with hydrochloric acid, is very readily precipitated by water. Of course this can be avoided by addition of tartaric acid. Ignited  $\text{Sb}_2\text{O}_4$  is not dissolved by sulphuric acid.

The above method of effecting the solution of meta-stannic acid is especially serviceable for analysing the residue left on acting on alloys by nitric acid. The residue is washed and heated with concentrated sulphuric acid in moderate quantity, till copious fumes are evolved. The solution (which should be quite clear) is allowed to cool, and is then treated with two or three times its bulk of concentrated hydrochloric acid, and boiled, if not still perfectly clear. In this solution the metals may be estimated by the usual methods. For their qualitative detection, I recommend dilution with about an equal bulk of water, and division into several portions.

1. The tin is detected by boiling (without further dilution) with metallic iron, and testing with mercuric chloride. The reduction to the stannous state is often perfect; antimony and copper are precipitated as metals; mere traces of tin may be detected.

2. After dilution, the presence of iron or copper is readily detected by potassium ferrocyanide.

3. The liquid is diluted, treated with tartaric acid, excess of ammo-



nia added, and phosphate or arseniate detected by magnesium. Streaks of arseniate are readily distinguished from phosphate by the method described by me in the *Chemical News* (vol. xxiv, page 120). Small quantities of arseniate are difficult of detection. Direct application of the molybdic acid test to the acid liquid usually indicates phosphate or arseniate when present, but the reaction seems uncertain.

4. The detection of antimony presents no difficulty.

The action of nitric acid on alloys of tin and gold produces a beautiful purple residue, which owes its colour to Purple of Cassius. This residue, when heated with concentrated sulphuric acid, is changed to a purplish liquid, which on further heating becomes colourless, the whole of the tin being dissolved, and the gold remaining as a heavy brown metallic residue. This curious reaction, I believe to be due to the formation of an unstable sulphate of gold, which is decomposed at a higher temperature, or by reaction with an equivalent amount of stannous sulphate. The residue was always washed quite free from nitric acid.

If hydrochloric acid be added before the purple solution decomposed, a small quantity of gold remains in permanent solution, probably as chloride. As a precaution against this source of error, if the solution has any yellow tint after addition of hydrochloric acid and an equal bulk of water, it is well to boil with a fragment of ferrous sulphate.

I had hoped from these results to obtain some insight into the obscure constitution of Purple of Cassius. The fact that it is formed by the action of nitric acid on an alloy of gold and tin, would seem to indicate the formula  $\text{Au}_2 + 3\text{SnO}_2 + 4\text{H}_2\text{O}$ , but its solubility in ammonia negatives this view, which is also at variance with the fact that mercury removes no gold from the colouring matter.

If we suppose the purple to contain  $\text{Au}_2\text{O}_3.3\text{SnO}.4\text{H}_2\text{O}$ , the fact of a purple liquid being formed with sulphuric acid is difficult to understand, if the oxides are merely converted into sulphates, as neither auric nor stannous sulphate has a deep colour, and they could scarcely co-exist in a liquid.

If the purple be regarded as containing aurous and stannous stannate ( $\text{Au}_2'\text{SnO}_3, \text{Sn}''\text{SnO}_3 + 4\text{aq.}$ ), the action of sulphuric acid would probably result in the formation of aurous, stannous, and stannic sulphates ( $\text{Au}_2'\text{SO}_4 + \text{Sn}''\text{SO}_4 + 2\text{Sn}^{\text{iv}}(\text{SO}_4)_2$ ), and at a higher temperature the aurous and stannous sulphates might easily react to form metallic gold and stannic sulphate, which are undoubtedly the ultimate products.

I have recently shown that auric sulphate is more stable than had been supposed,\* and although aurous sulphate has never been obtained, it may possibly exist and possess a purple colour like the aurous stan-

\* See page 285.

nate supposed to be present in the Purple of Cassius. Aurous oxide is stated by Figuier to have a violet colour, and to combine with acids. On diluting the sulphuric solution with water, the purple is gradually deposited in an apparently unchanged state.

I do not believe the purple solution can owe its colour to suspended gold.

I have found the sulphuric acid method especially serviceable for the qualitative and quantitative analysis of dentists' alloys containing gold, silver, and tin. After obtaining the nitric acid residue, and thus separating the silver, the gold and tin are acted on with sulphuric and hydrochloric acids as before described, the gold being weighed direct, and the usual methods applied to the estimation of the tin in the solution. For this purpose I prefer to neutralise the free acid, add a moderate excess of sulphuric acid, dilute largely and boil, when the whole of the tin is thrown down as a white precipitate of meta-stannic hydrate, which can be readily filtered and washed.

The purity of the gold was ascertained by dissolving it in bromine water, which in every case effected complete solution.

By the above method all residues left by the action of nitric acid on alloys can be rapidly and accurately analysed in the wet way, thus avoiding all processes of fusion or ignition.

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# ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

## Physical Chemistry.

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### Use of Potassium Permanganate in the Galvanic Battery.

By J. H. KOÖSEN (Pogg. Ann., cxliv, 627-638).

THE author states that in a cell constructed like that of Grove's battery, but using potassium permanganate instead of nitric acid, an electromotive force equal to 2 or 2.1 (a Daniel cell = 1) can be obtained. The construction of the cell recommended by the author is as follows:

If a constant current be desired, a well amalgamated zinc cylinder is taken, inside of which is placed a smaller cylinder, made of hair cloth, which is about 1 centim. higher than the zinc cylinder. The platinum plate is made by placing together several quadrangular sheets of very thin foil, of such a size as easily to fit into the hair-cloth cylinder; these pieces are held together on one side by two thin gold wires; a platinum wire, serving as an electrode, is also fastened on the same side, and then the pieces of foil are separated out into the form of a fan, which is placed within the hair-cloth cylinder, this latter serving to prevent contact between the zinc and platinum.

The whole arrangement is now filled up with water acidified with  $\frac{1}{10}$ th volume of sulphuric acid. In a small platinum sieve, just covering the hair-cloth cylinder, and dipping about 1 centim. into the liquid, 20 to 30 grm. *pure* crystallised potassium permanganate are placed. In a few minutes the arrangement is in full work, and if assistance equal to 30 metres of normal copper wire be introduced, a constant and powerful current is obtained.

As compared with a Grove cell, which the author takes at about 1.58, this arrangement gives an electromotive force of 2, with a very small internal resistance.

For such purposes as regulating clocks, electric bell-ringing, &c., the author recommends the use of a porous cell, just as in Grove's arrangement, into which water with  $\frac{1}{10}$  sulphuric acid is placed, 40-50 grm. potassium permanganate being put into the platinum sieve, or instead of this sieve, a small glass flask, with a short neck, dipping a little way into the solution may be used, into which 100 grm. permanganate may be thrown, and the flask filled up with water.

M. M. P. M.

### Resounding Flames. By H. PLANETH (Pogg. Ann., cxliv, 639).

WHEN a tuning-fork in vibration is brought near a flame, a loud tone is suddenly perceived, which, in the case of a rapidly burning gas-flame, is quite as loud as that produced by placing the foot of the fork upon a sounding-board. The loudest tone is produced by bringing



the flame between the prongs of the vibrating fork. By turning the fork as it approaches the flame, there occurs at four points during a revolution a sensible diminution of the tone due to interference. If the flame is burning unsteadily, the tone acquires a tremulous character, which disappears when the fork is brought near to the lower and steadily burning portion of the flame. This effect is doubtless due to resonance, the entire phenomenon being nearly related to that of the singing flame.

T. E. T.

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**Spectrum of the Vapour of Water.** By J. JANSSEN (Ann. Chim. Phys. [4], xxiv, 215-217).

M. JANSSEN has observed the absorption-spectrum produced by aqueous vapour. In order to obtain a sufficient length of the absorbing medium, an iron tube 37 metres long was taken and placed in a wooden case, containing well dried saw-dust. The steam was generated in a boiler of six-horse power, the source of light being a row of six gas jets, placed in the axis of the tube. In one experiment the tube was filled with steam at a pressure of 7 atmospheres, when the spectrum showed 5 dark bands (two of them well marked) distributed from D to A, almost resembling the spectrum of the setting sun as viewed in the same instrument. A small drawing is given of the spectrum showing that the group  $\alpha$ , a great part of B, group C, and two groups between C and D, are due to the action of the aqueous vapour in our atmosphere. This, it will be seen, accounts for a considerable number of the Fraunhofer lines.

A. P.

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**Absorption Spectra produced by Solutions of Nitrogen Tetroxide, Chlorine Tetroxide, and Chlorine Trioxide.** By D. GERNEZ (Compt. rend., lxxiv, 465-468).

THE absorption spectrum of liquid nitrogen tetroxide was found to be similar to that of the gas, though considerably more intense. The author then examined the solutions of this gas in benzene, nitrobenzene, carbon disulphide, and chloroform (in which the gas dissolves without alteration), all of which gave the same absorption bands as the liquefied gas. Mixtures of nitric acid and nitrogen tetroxide do not show the same spectrum even when the proportion of liquid nitrogen tetroxide amounts to one-third of the weight. If carbon disulphide is added to the mixtures, it dissolves out the nitrogen tetroxide, and shows the absorption bands, as above.

The absorption spectrum of chlorine tetroxide consists of several bands in the blue and violet. The gas itself and its solution in chloroform show the same spectrum.

Chlorine trioxide (chlorous anhydride) gives a total absorption of the blue and violet up to the green in the spectrum; very dilute solutions, however, show that this is made up of several absorption bands.

A. P.

## Inorganic Chemistry.

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**Decrease in Chemical Activity of Hydrogen and Carbon Monoxide in the reduction of Ferroso-ferric Oxide, by admixture with Foreign Gases.** By W. MÜLLER (Pogg. Ann., cxliv, 609—626).

THE author first refers to the memoirs of Deville upon the action of a mixture of steam and hydrogen upon metallic iron and ferric oxide, in which that chemist shows:—

1. That the increase in the tension of hydrogen formed by the action of steam upon iron is a continuous phenomenon, when the tension of the steam is made to vary progressively, and the temperature of the iron remains constant.

2. That the tension of the hydrogen, corresponding to an invariable tension of steam, decreases continuously, when the temperature increases progressively.

3. That the same laws are observed in the inverse phenomenon of the reduction of ferric oxide by hydrogen.

These conclusions are substantially identical with results obtained by Müller in 1867 and 1868. From a fresh series of experiments he draws the following conclusions:—

1. A mixture of iron and ferroso-ferric oxide, heated to a certain temperature in an atmosphere of aqueous vapour and hydrogen, or of carbon monoxide and carbon dioxide, gives rise to a constant proportion in the amounts of the two gases, and is afterwards no longer altered thereby.

2. This mutual action of gases having no chemical action upon one another is a general phenomenon.

3. The action of various admixed gases is not dependent upon their specific gravities alone, but varies with their specific nature.

T. E. T.

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**New Observations on the alternate predominance of Nitrous and Nitric Acid in Rain Water.** By M. CHABRIER (Compt. rend., lxxiii, 1273).

As the result both of recent and of former observation, the author finds that the ratio of nitrous to nitric acid in rain-water depends upon the degree of heat, moisture, and electricity of the atmosphere. The conditions favourable to the production of nitrous acid are calm and cloudy weather, a mean temperature, and an elevated hygrometric condition; while, on the other hand, the production of nitric acid is

favoured by a high temperature, a dry atmosphere, high winds, and thunder-storms.

J. W.

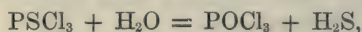
**Decomposition of Phosphoric Sulphobromide by Water and Alcohol.** By A. MICHAELIS (Deut. Chem. Ges. Ber., v, 4).

THE products of the decomposition of  $\text{PSBr}_3$  by water are—sulphur, hydrogen sulphide, hydrobromic, phosphorous, and phosphoric acids (last volume of this Journal, p. 1163). As result of a quantitative experiment the author finds that 28.01 per cent. are decomposed into hydrogen sulphide and phosphoric acid, and 71.99 per cent. (about  $2\frac{1}{2}$  times as much) into sulphur and phosphorous acid.

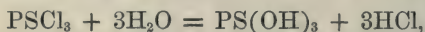
The action of alcohol is far simpler, the compound  $\text{PS}(\text{OC}_2\text{H}_5)_3$  being formed.

The explanation of the somewhat remarkable action of water is probably furnished by the behaviour of sulphophosphoric acid, which, according to Wurtz, when liberated by the action of acids on the salt  $\text{PS}(\text{ONa})_3$  (readily obtained by boiling  $\text{PSCl}_3$  with soda), at once decomposes into hydrogen sulphide and phosphoric acid. The author finds, however, that sulphur and phosphorous acid are also invariably produced.

The decomposition of phosphoric sulphochloride (and bromide) by water, therefore, evidently takes place simultaneously in two ways. In a portion sulphur is first replaced, thus:—



and the phosphoric chloride is at once further decomposed into phosphoric and hydrochloric acids. In another portion chlorine (or bromine) is replaced, thus:—



the sulpho-phosphoric acid yielding in its turn the above-mentioned decomposition products.

H. E. A.

**Phosphoric Bromochloride.** By A. MICHAELIS (Deut. Chem. Ges. Ber., v, 9).

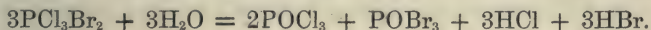
ACCORDING to Wichelhaus,  $\text{PCl}_3$  and  $\text{Br}_2$  unite, with evolution of heat, to form a compound which crystallises in a freezing mixture, but which at ordinary temperatures separates into two liquid layers; and he considers that the compound is broken up on liquefaction just as  $\text{PCl}_5$  is resolved into  $\text{PCl}_3 + \text{Cl}_2$  when vaporised.

The author finds  $\text{PCl}_3\text{Br}_2$  to be a body of considerable stability, even at ordinary temperatures. The combination takes place but slowly; and when phosphorous chloride and bromine are first mixed, a liquid is obtained, consisting of two layers—solutions respectively of phos-



phorous chloride in bromine, and of bromine in phosphorous chloride. In a freezing mixture at  $-20^{\circ}$  this liquid solidifies, but again separates into two layers on fusion. If, however, the mixture be allowed to remain undisturbed in a sealed tube at winter temperature for about a week, a crystalline mass is obtained which does not form two layers again at ordinary temperatures, but a homogeneous liquid.

Phosphoric bromochloride is a yellowish red mass resembling phosphoric bromide. At  $35^{\circ}$  it is resolved into  $\text{PCl}_3$  and  $\text{Br}_2$ . Water has the same action upon it as upon a mixture of phosphorous chloride and bromine (*Zeitschr. f. Chem.*, vii, 158);



H. E. A.

**Phosphoric Sulphobromochloride.** By A. MICHAELIS (*Deut. Chem. Ges. Ber.*, v, 6).

This body is prepared by the action of bromine upon the ether  $\text{PCl}_2(\text{SC}_2\text{H}_5)$ .

*Ethylsulphophosphorous Chloride*,  $\text{PCl}_2(\text{SC}_2\text{H}_5)$ .—On slowly adding mercaptan (1 mol.) to phosphorous chloride (1 mol.), reaction takes place quietly, but almost the whole of the hydrochloric acid formed is absorbed. The products are  $\text{PCl}_2(\text{SC}_2\text{H}_5)$  and  $\text{P}(\text{SC}_2\text{H}_5)_3$ , a considerable quantity of the latter being obtained.

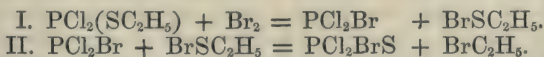
It is a colourless liquid, of sp. gr. 1.30 at  $12^{\circ}$ , boiling at  $172^{\circ}$ — $175^{\circ}$ , and decomposed by water into mercaptan, phosphorous and hydrochloric acids. It has a penetrating odour, somewhat resembling that of mercaptan.

*Sulphophosphorous ether*,  $\text{P}(\text{SC}_2\text{H}_5)_3$ , is a colourless liquid, which boils between  $240^{\circ}$ — $280^{\circ}$ . Its odour is unpleasant, but does not resemble that of mercaptan. Water decomposes it slowly into mercaptan and phosphorous acid.

$\text{PSClBr}$  was prepared by slowly adding bromine (1 mol.) to  $\text{PCl}_2(\text{SC}_2\text{H}_5)$  (1 mol.). The product was shaken with water so long as perceptible action occurred, dried over calcium chloride, and freed from dissolved hydrochloric and hydrobromic acids by warming gently. The product thus purified gave satisfactory numbers on analysis.

It cannot be distilled unchanged, but is acted upon by water only with difficulty, and may even be partially distilled in a current of steam. Its complete decomposition is effected only by heating in sealed tubes to  $150^{\circ}$ . The products are sulphur, hydrogen sulphide, phosphorous, phosphoric, hydrochloric, and hydrobromic acids. Only half as much sulphur, however, is obtained as in the analogous decomposition of  $\text{PSBr}_3$  by water.

The author considers that the formation of this body probably takes place by two stages, thus:—



He finds that  $\text{P}_2\text{S}_3$  and bromine unite readily to form  $\text{P}_2\text{S}_3\text{Br}_4$ ,

the ether of which,  $P_2S_3(OC_2H_5)_4$ , has been obtained. He regards this compound as pyrophosphoric sulphobromide,  $\begin{cases} PSBr_2 \\ S \\ PSBr_2 \end{cases}$ .

H. E. A.

### Supersaturation of Sodium Chloride Solution.

By L. DE COPPET (Compt. rend., lxxiv, 328).

IN examining this phenomenon, observed by Blagden in 1788, and since then by Schroeder, the author cools by a freezing mixture a solution of sodium chloride, saturated cold in an open vessel exposed to dust, and constantly agitated with an excess of solid sodium chloride. At a temperature some degrees higher than the freezing point of the liquid normally saturated, the whole solidifies, from formation probably of the hydrate,  $NaCl \cdot 2H_2O$ . This compound, therefore, though very unstable at ordinary temperatures, and instantly decomposed by contact with the ordinary salt, appears to be permanent at temperatures below  $0^\circ$ . Moreover, the presence of the solid salt does not prevent supersaturation.

A solution saturated hot, and containing 36.4 per cent. of ordinary chloride, on cooling to  $-14^\circ$ , suddenly formed a mass of transparent crystals, the thermometer rising to  $1^\circ$ — $1.5^\circ$ , to fall again slowly to  $-14^\circ$ . The mother-liquor contained 32.5 per cent. of anhydrous chloride. Another portion left in the air also crystallised suddenly, though the temperature had risen considerably. The mother liquor at  $0^\circ$  contained 35.7 per cent. of anhydrous salt. These numbers agree with those given by Mulder and Poggiale, as to the solubility of sodium chloride, but they evidently belong to the hydrate, and not to the anhydrous substance. The facility of supersaturation explains why some authors state the solubility to be the same for all temperatures, and others that it is greater at  $0^\circ$ .

C. G. S.

### Action of Low Temperatures on Supersaturated Solutions of Glauber's Salt. By CHARLES TOMLINSON, (Proc. Roy. Soc., xx, 109).

A SOLUTION of one to three parts of the ordinary ten-atom hydrate of sodium sulphate in one part of water is boiled and filtered into a closed flask previously cleaned by strong nitric acid and water. When cool, the flask is placed in a freezing mixture. At about  $-6^\circ$  opaque white crystals of a new hydrate are formed, the thermometer rising to  $-3^\circ$ . After a time the temperature suddenly rises to about  $10^\circ$ , the whole solidifying as the ordinary salt. The rise in temperature is not dependent on the mass. Any of the usual transparent octohedrons of the anhydrous salt that may have formed in the cooling become opaque at  $-3^\circ$ . The new hydrate may appear in tufts of regular octohedrons, breaking up into a woolly mass in fern-like crystalline forms, or, if much shaken, as an amorphous deposit. M. Violette alone has slightly noticed the new compound as "crystallising in the form of

cauliflowers." The anomalies of Löwel's results were due to his not then understanding the conditions of clean and unclean in his vessels.

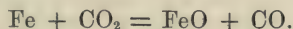
A supersaturated solution of potash alum in a freezing mixture develops foliate crystals, which melt at  $0^{\circ}$ , giving a clear supersaturated solution as before.

C. G. S.

### **New Method of producing the Anhydrous Protoxide of Iron.**

By G. TISSANDIER (Compt. rend., lxxiv, 531).

THE anhydrous protoxide of iron is procured by acting on pure iron heated to redness with carbonic acid. The reaction takes place according to the formula:—



The oxide thus obtained is black, brilliant, and crystalline. It is also magnetic. On analysis it gave 77.69 per cent. of iron, the calculated number being 77.77. Heated to redness in contact with air, it absorbs oxygen, forming the oxide  $\text{Fe}_3\text{O}_4$ .

S. W.

### **The Solubility of Gold, and the Stability of Auric Nitrate and Sulphate.** By ALFRED H. ALLEN (Chem. News, xxv, 85).

It is stated by Gmelin, and other competent authorities, that a solution of auric oxide in nitric or sulphuric acid, is rapidly and completely decomposed on dilution with water. The experiments of the author, although not instituted with the intention of directly refuting the above statement, clearly show that the oxacid salts of gold are more definite and more stable in solution than they are usually supposed to be.

A solution of auric oxide in nitric acid gave a perfectly clear solution on dilution with water, which answered to all the tests for gold. It decomposed very gradually by keeping, the oxide being deposited.

In like manner, an aqueous solution of auric sulphate deposited but very slowly a portion of the metal, the decomposition in many instances being very slight, and never wholly complete, even after a long interval.

Finely divided gold, when heated with solid potassium permanganate and concentrated sulphuric acid, is rapidly dissolved, yielding a solution which is not precipitated at all on dilution, but gives when tested with oxalic acid or ferrous sulphate, abundant evidence of the presence of gold. There would appear then to be no doubt that the gold exists in this solution in the state of sulphate.

When nitric acid is substituted for sulphuric acid, the gold is completely precipitated on the addition of water. Messrs. Reynolds and Spiller are of opinion that in this latter reaction, auric sulphate is not produced. The author objects to this conclusion, and points out that



the true cause of the reduction is the presence in the solution of nitrous acid, since, if a small quantity of permanganate be added before dilution, or if the acid liquor be boiled with a crystal of ammonium sulphate, precipitation of the gold does not take place.

This explanation is further strengthened by the fact that it is possible, by adding a few drops of fuming acid to a pure solution of auric nitrate, to cause an instantaneous precipitation of the metal.

J. W.

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**A Study of certain Tungsten Compounds.** By HENRY E. ROSCOE (Proc. Manch. Lit. Phil. Soc., Jan. 23, 1872, and Chem. News, xxv, 61, 73).

THE following research was undertaken in order to establish definitely the constitution of the tungsten compounds. Until recently, the atomic weight of tungsten, as ascertained by Berzelius, was generally accepted; but the experiments of Persoz and Debray had thrown some little doubt upon the accuracy of the reasoning on which this atomic weight was based; and the former chemist, upon the assumption that the metal functioned as a pentad and not as a hexad element, had reduced the atomic weight from 184 to 153.

This latter number was singularly corroborated by the determination of the vapour-density of tungsten chloride by Debray, who found that the experimental density corresponded very closely with that calculated from the formula  $TuCl_6$ , where  $Tu = 153$ .

The author takes up the subject at this point, and in the course of the investigation adduces evidence to prove that the vapour-density of the chloride, as ascertained by Debray, was abnormal, and that the atomic weight is not at variance with the normal atomic heat.

*Tungsten Hexchloride.*—Metallic tungsten when heated, takes fire in chlorine and produces a granular sublimate of dark violet crystals of the hexchloride. When pure, the solid hexchloride melts at  $275^\circ$ , and boils at  $346.7^\circ$ ; at the ordinary temperature it undergoes no change, even in moist air; but if the smallest trace of oxychloride be present, it rapidly absorbs moisture, and decomposes. It is readily soluble in carbon disulphide.

The analysis was effected by decomposing the salt with water, and reducing the oxide so obtained in a current of hydrogen (the latter operation being imperative), on account of the persistence with which tungstic acid retains chlorine; the total hydrochloric acid was collected and estimated in the usual manner. The results of six analyses gave a mean percentage which agrees accurately with the percentage calculated from the formula  $WCl_6$ .

The vapour-density of the hexchloride determined at  $440^\circ$  gave a result which coincided with the experiments of Debray, and was therefore considerably too low if 184 be taken as the atomic weight of tungsten; at  $350^\circ$ , however, the density became normal; from this fact it is argued that at the higher temperature dissociation takes place; and inasmuch as it was found that when the chloride was distilled at a high temperature in a current of carbonic anhydride, a

considerable quantity of free chlorine was liberated, it would certainly seem more reasonable to explain the anomalous vapour-density by dissociation, than by the suggestion of an error in the atomic weight.

*Tungsten Pentachloride.*—This compound was prepared by partially reducing the hexchloride at a low temperature in a current of hydrogen, and then distilling off the volatile pentachloride from the non-volatile tungsten compounds containing less chlorine, formed at the same time. It crystallises in black, shining, highly deliquescent needles, which melt at  $248^{\circ}$ , and boil at  $275\cdot6^{\circ}$ . Its vapour-density and percentage composition correspond with the formula  $WCl_5$ .

*Tungsten Tetrachloride and Dichloride.*—The tetrachloride,  $WCl_4$ , forms the non-volatile residue produced in the distillation of the hexchloride in hydrogen, provided that the temperature has not been allowed to rise too high. It is a soft, crystalline, highly hygroscopic powder, of a greyish-brown colour: is decomposed, when strongly heated, into the volatile pentachloride and a lower dichloride which remains behind. The latter chloride is a loose grey powder, without lustre or crystalline structure. The results of its analysis calculated to the formula  $WCl_2$ .

*Tungsten Oxychlorides.*—The monoxychloride,  $WOC l_4$ , was obtained by passing the vapour of a chloride over the heated oxide or dioxychloride in a current of chlorine. It occurs in beautiful ruby-red crystals, which melt at  $210\cdot4^{\circ}$ , and volatilise at  $227\cdot5^{\circ}$ , and on exposure to air become at once coated with a yellow crust of the dioxychloride. The author obtained perfectly normal results in the determination of the vapour-density of this oxychloride; a result which is in opposition to the experiments of Debray.

The dioxychloride was prepared by passing chlorine over the brown dioxide. It corresponds with the formula  $WO_2Cl_2$ .

*Tungsten Bromides.*—By the action of excess of bromine on tungsten, a penta- and not a hexbromide is obtained. The crystals of the pentabromide possess a dark metallic lustre, resembling iodine; they undergo a slight decomposition by keeping, bromine being liberated. Analysis corroborated the formula  $WBr_5$ . When the pentabromide is heated to  $350^{\circ}$  in a current of hydrogen, the dibromide,  $WBr_2$ , is produced. Some slight indication of the formation of the compound  $WBr_3$  was also observed, but the author failed to isolate it.

*Tungsten Oxybromides.*—The oxybromides closely resemble the oxychlorides, and are prepared in a similar manner. The formulæ,  $WOB r_4$  and  $WO_2Br_2$ , agree with the analytical results.

*Tungsten Iodide,  $WI_2$ .*—Tungsten appears to form but one compound with iodine, the diiodide, which is produced when iodine vapour is passed over heated metallic tungsten, or over the brown oxide. It is a somewhat unstable compound, losing its iodine when heated in the air, and becoming converted into tungstic acid.

*Atomic Weight of Tungsten, determined: 1. By reduction of the Trioxide.*—In order to prepare tungstic acid free from alkali, the pure oxychloride was decomposed with water, and the resulting oxide washed, dried, and ignited in platinum, contact with glass being detrimental to the accuracy of the experiment. The loss of weight, by reduction in hydrogen, and the gain of weight on oxidation, was several times



repeated. As a mean of the experiments, the number 183·84 was calculated as the atomic weight.

2. *By Analysis of the Hexchloride.*—The hexchloride employed was quite free from pentachloride and oxychloride, and yielded a beautiful canary-yellow trioxide on treatment with water. The percentage obtained was  $\text{Cl} = 53\cdot605$ ,  $\text{W} = 46\cdot368$ , which gives as the atomic weight, 184·25. Taking the mean of the two methods, 184·04 is considered as the correct atomic weight of tungsten.

J. W.

## Mineralogical Chemistry.

**The Chemical Composition of the Sodio-calcic Felspars; a Contribution to the Theory of Isomorphism.** By G. VOM RATH (Pogg. Ann., cxliv, 219—260).

THIS paper contains the crystallographic description and chemical analysis of nine sodio-calcic felspars from different localities, all tending to support the theory first enunciated by Sartorius v. Waltershausen, and afterwards worked out by Tschermak, Rammelsberg, and Streng (p. 50 of this volume), that there are but two distinct species of triclinic felspar or plagioclase, viz., albite and anorthite, the former being a pure soda felspar,  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ , the latter a pure lime felspar,  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ; and that the intermediate minerals, namely, oligoclase, andesin, and labradorite, formerly regarded as distinct species, are in reality isomorphous mixtures of these two, approaching to the one or the other accordingly as the soda or the lime predominates in their composition. The chief chemical argument in favour of this view is that, in all the calcio-sodic felspars, an increase in the lime is attended with an increase of the alumina and a decrease of the silica, while, on the other hand, an increased proportion of soda is attended with a diminution of the alumina and an increase of the silica; and that a definite proportion of lime to soda corresponds in all cases to a definite amount of silica.

The felspars examined by vom Rath are:—

a. *Andesin from Vesuvius*; identical in crystalline form with the formerly-described oligoclase from the same locality.

b. *Oligoclase from Niedermendig.*

c. *Oligoclase* from a tourmalin-rock in the Veltlin, forming a coarse-grained mixture of black tourmalin and quartz. The oligoclase appears in crystalline grains an inch in diameter, having a bluish-white colour and a fine, distinct striation on the face *P*.

d. *Andesin* from the hornblende-melaphyre of Monte Mullatto, near Predazzo; very distinctly striated on *P*.

e. *Andesin* from the diorite-porphyr of Fréjus (Dep. du Var).

f. *Labradorite* from the diorite of the Veltlin, a coarse-grained mixture of distinctly striated plagioclase and blackish-green hornblende. The labradorite is bluish-white, and translucent when fresh; snow-white when somewhat decomposed.



*g. Labradorite* from the porphyrite of the Tannbergthal (near Schöneck in the Saxon Voigtland). Nearly transparent and colourless crystals, sometimes 3 centim. long, accompanied by red orthoclase, roundish red quartz-grains, and iron pyrites.

*h. Labradorite* from the dolerite of Hafnefjord in Iceland. This mineral which, together with augite, constitutes a doleritic lava, the so-called Klöftlava of Iceland, was called *Hafnefjördite* by Forchhammer, who regarded it as a distinct species; but his analysis, which gave 61·2 p. c. silica to 8·8 p. c. lime, appears to have been made on an impure specimen.

*i. Plagioclase* (oligoclase) from the basalt of the Hartenberg in the Siebengebirge. This felspar, which contains a much larger proportion of potash than any of the preceding, may be regarded either as a mixture of albite (8 mol.), anorthite (3 mol.), and orthoclase (3 mol.), or of 3 mol. of an albite rich in potash and 1 mol. anorthite.

The following table contains the results of the analysis of the nine calcio-sodic felspars above specified. The small figures denote the percentages of silica, &c., as calculated from the formulæ:—

*Composition of Sodio-calcic Felspars.*

	Specific gravity.	Silica.	Alumina.	Lime.	Potash.	Soda.	Magnesia.	Ferric oxide.	Total.	Ratio of molecules of Albite : Anorthite.	Formula.
<i>a</i> ..	2·647	58·53 58·48	26·55 26·49	6·43 8·02	0·89	7·74 7·01	—	—	100·14	4 5	$\text{Na}_8\text{Ca}_5\text{Al}_{18}\text{Si}_{34}\text{O}_{104}$ .
<i>b</i> ..	2·611	53·06 63·23	23·27 23·22	4·16 4·22	0·62	8·93 9·33	—	—	100·03	2 1	$\text{Na}_4\text{CaAl}_6\text{Si}_{14}\text{O}_{40}$ .
<i>c</i> ..	2·632	64·58 64·12	23·08 22·62	3·49 3·52	0·62	8·98 9·74	—	—	100·65	5 2	$\text{Na}_{10}\text{Ca}_2\text{Al}_{14}\text{Si}_{34}\text{O}$ .
<i>d</i> ..	2·663	60·35 59·73	25·45 25·59	5·14 6·97	1·21	7·63 7·71	0·03	—	99·81	1 1	$\text{Na}_2\text{CaAl}_4\text{Si}_8\text{O}_{24}$ .
<i>e</i> ..	2·636	58·03 58·48	26·64 26·49	8·07 8·02	0·97	6·16 7·01	—	—	99·87	4 5	$\text{Na}_8\text{Ca}_5\text{Al}_{18}\text{Si}_{34}\text{O}_{104}$ .
..	2·690	55·25 55·43	29·15 28·49	9·90 10·35	0·80	5·23 5·73	—	—	100·23	1 2	$\text{Na}_2\text{Ca}_2\text{Al}_6\text{Si}_{10}\text{O}_{32}$ .
<i>g</i> ..	2·711	53·61 54·02	29·68 29·45	10·96 11·46	1·15	4·36 5·07	—	—	99·76	2 5	$\text{Na}_4\text{Ca}_5\text{Al}_{14}\text{Si}_{22}\text{O}_{72}$ .
<i>h</i> ..	2·729	54·23 54·02	29·64 29·45	12·01 11·46	trace	4·41 5·07	0·11	—	100·40	2 5	$\text{Na}_4\text{Ca}_5\text{Al}_{14}\text{Si}_{22}\text{O}_{72}$ .
<i>i</i> ..	2·632	63·58 63·93	21·81 21·90	2·32 2·98	3·65	6·84 7·45	0·25	0·66	99·81	3 1	$\text{K}_3\text{Na}_9\text{Ca}_2\text{Al}_{16}\text{Si}_{40}\text{O}_{112}$ .

H. W.

**Contributions to Mineralogy.** By G. VOM RATH (Pogg. Ann., cxliv., 375—395 and 594—596).

1. *Chemical Composition of certain Orthoclases.*—*a.* From Bolton in Massachusetts.—This felspar is accompanied by large crystals of green augite and brown titanite. The surface of the crystals is rough, drusy,

and of a yellowish colour, the interior pure white, semi-transparent. The cleavage-faces *P* and *M* are slightly curved, but without any trace of twin striation or albite lamellæ; colour and lustre similar to those of adularia. Sp. gr. 2.586. Loss by ignition 0.05 p. c.

A very similar felspar, accompanied by fine crystals of augite, scapolite, and titanite, is found in the neighbourhood of Diana, Lewis City, New Jersey.

*b. From Pargas in Finland*, also accompanied by augite. The crystals are sometimes 2 centimeters long, but mostly much smaller. They are white, and covered with a dull white crust of milky aspect. The edges are rounded. Sp. gr. 2.576. Loss by ignition 0.13 p. c.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.
<i>a</i> ..	65.23	19.26	0.42	—	11.80	2.98= 99.69
<i>b</i> ..	64.96	19.40	0.49	0.25	12.80	2.32=100.22

Both analyses agree nearly with the composition of an orthoclase containing 3 at. K to 1 at. Na (or a mixture of 3 mol. potash felspar to 1 mol. albite), which requires 65.58 SiO<sub>2</sub>, 18.73 Al<sub>2</sub>O<sub>3</sub>, 12.87 K<sub>2</sub>O, and 2.82 Na<sub>2</sub>O.

The two following orthoclastic felspars exhibit abnormal composition, and should perhaps be regarded as mixtures of orthoclase, albite, and anorthite.

*c. Felspar from the Syenite of Laurvig.*—This mineral is the principal constituent of the remarkable rock which extends along the coast of Norway from the Langesund-fjord to the Christiania-fjord. The crystals of the felspar are bluish to brownish-grey, and exhibit a composite structure. A thin section parallel to *P* appears, even by ordinary light, as an intimate combination of curved lamellæ, exactly like the intergrowth of orthoclase and albite exhibited in perthite. In polarised light this striation of the surface is much more evident, the lamellæ which are inserted nearly parallel to the orthopinacoid exhibiting a variety of brilliant colours. Sp. gr. 2.619. Loss by ignition 0.31. Analysis gave numbers agreeing approximately with a mixture of 1 mol. orthoclase, 3. mol. albite, and 2 mol. anorthite:—

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.
Analysis ....	62.81	23.21	2.60	0.07	4.23	7.54=100.46
Calculation ..	62.48	22.94	4.16	—	3.50	6.92=100

*d. Felspar from the Syenite of Monte Monzoni* (Toal, near Rizzoni), Fassa. Forms the predominating constituent of this beautiful coarse-grained rock, which in some places may be regarded as a more or less pure feldspathic rock. The light-grey felspar occurs in grains  $\frac{1}{2}$  to 2 centimeters in diameter, together with small quantities of black hornblende, and a very few small granules of titanite. Microscopic examination in polarised light showed that this felspar also contains a quantity of small grains of plagioclase embedded in its substance. No striation was however visible, the granules of plagioclase being merely intergrown with the orthoclase in parallel directions, but otherwise irregularly. Sp. gr. 2.565. Loss by ignition 0.89 p. c. (the mineral splits when ignited).

Analysis gave the following numbers, agreeing closely with the composition of a mixture of 5 mol. orthoclase, 4 mol. albite, and 2 mol. anorthite:—

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.
Analysis . . . .	63·36	21·18	1·66	8·89	4·91 = 100
Calculation ..	63·96	20·78	2·06	8·65	4·55 = 100

The somewhat considerable quantity of lime is accompanied, as in the Laurvig felspar, by an increase in the proportion of alumina and a decrease in that of the silica, which is in accordance with the supposition that the plagioclase mixed with these felspars is a mixture of albite and anorthite. Other orthoclastic felspars, loxoclase for example, containing lime with a large proportion of soda, are probably constituted in a similar manner.

2. *Ersbyite from Pargas*.—Occurs intergrown with blackish-green augite (in small quantity) and brown titanite, in some parts also with laminar calcspar. It is colourless when quite fresh, and does not exhibit any crystalline faces. Its specific gravity is 1·723.

Considerable uncertainty has hitherto existed respecting the constitution of this mineral. A. E. Nordenskjöld described it as a triclinic felspar, cleavable in two directions, inclined to one another at an angle of 90° 22', and according to an analysis made by N. A. Nordenskjöld (54·13 SiO<sub>2</sub>, 29·23 Al<sub>2</sub>O<sub>3</sub>, 15·46 CaO, 1·07 water) as a true labradorite free from soda. But according to the theory of Tchernmak, which regards the triclinic felspars as isomorphous mixtures of albite and anorthite (pp. 50, 288), there should be no such thing as an oligoclase free from lime, or a labradorite free from soda.

To clear up this doubt, vom Rath has subjected the mineral to a fresh examination. He finds that it cleaves very distinctly and with equal precision in two directions at right angles to each other. Sp. gr. 1·723. Loss by ignition 0·58 p. c. Gives by analysis—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.
44·26	30·37	20·17	0·15	1·15	2·75 = 98·85

If the loss in the analysis be attributed to lime and the alkalis, these numbers agree very nearly with the formula of scapolite  $3\left(\frac{7}{8}\text{CaO}\right) \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$  (calc. 44·39 SiO<sub>2</sub>, 30·4 Al<sub>2</sub>O<sub>3</sub>, 21·75 CaO, and 3·44 Na<sub>2</sub>O).

Both the cleavage and the chemical composition of ersbyite show, therefore, that it belongs, not to the calcio-sodic felspars, but to the scapolites.

3. *Occurrence of Sahlite* (calcio-magnesio-ferrous augite) *in the Pennine Alps*.—This mineral occurs, together with graphite, in some of the dense limestones imbedded in the mica- and hornblende-slate of Valpellina. The augite forms rounded grains having a fused appearance, generally from  $\frac{1}{2}$  to 1 mm. in size, and of a bluish colour on the outside, whitish-grey within. Some of these grains exhibit crystalline



faces, namely, those of the vertical prism of augite, and of the ortho- and clinopinacoid. They exhibit distinct cleavage in two directions, parallel to the faces of the vertical prism, indistinct in one direction, corresponding to the clinopinacoid. Before the blowpipe, the mineral melts easily, and with violent intumescence. Sp. gr. = 3.329. Loss by ignition 0.14 p. c. Analysis gave—

SiO <sub>2</sub> .	CaO.	MgO.	FeO.	Al <sub>2</sub> O <sub>3</sub> .
54.02	24.88	13.52	8.07	0.20 = 100.69

which, neglecting the alumina, agrees nearly with the formula ( $\frac{1}{3}$ FeO,  $\frac{2}{3}$ MgO .  $\frac{1}{2}$ CaO)SiO<sub>2</sub>, or FeMg<sub>3</sub>Ca<sub>4</sub>Si<sub>8</sub>O<sub>24</sub> (calc. 53.57 SiO<sub>2</sub>, 25.00 CaO, 13.39 MgO, 8.04 FeO).

4. *An interesting Eruptive Wollastonite from Monte Somma.*—The rocky masses in which wollastonite is found are generally aggregates of light green mica, augite, garnet, and limestone, sometimes also containing leucite. In other masses wollastonite and melanite (calcio-ferric garnet) form a coarse-grained mixture, which is one of the most beautiful of the Somma rocks. In these cases the wollastonite may be supposed to have been formed—like garnet, vesuvian, mejonite, anorthite, &c.—by volcanic action, from the masses of limestone which are so abundantly mixed with the tufa of Somma. This view is confirmed by the author's examination of a mineral ejected from Somma, and consisting of a nucleus of compact limestone coated with a crust of wollastonite 25 mm. thick, arranged in parallel layers perpendicular to the circumference. There is abundant evidence that this crust of wollastonite originally surrounded the entire mineral. A zone of the limestone just beneath the crust is filled with little crystals of wollastonite, and this same zone is continued of the same thickness round to the other side, where there is no longer any crust. Crystals of wollastonite likewise occur in the central part of the mass, but less thickly than in the zone just mentioned.

The wollastonite in the crust, when freed by acetic acid from calcium carbonate, had a sp. gr. of 2.853. Its analysis gave—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Loss by ignition.
51.31	1.37	45.66	0.73	0.75 = 99.82,

agreeing nearly with the formula CaO.SiO<sub>2</sub>, or CaSiO<sub>3</sub>, which requires 51.72 silica and 48.28 lime.

The peripheral mass of the limestone near the outer crust yielded to acetic acid 41.51 p. c. of soluble matter (calcium carbonate), and therefore 58.49 p. c. wollastonite. The central portion yielded 74.67 p. c., soluble in acetic acid, and therefore 25.33 wollastonite.

From all this it is evident that the conversion of the calcium carbonate into silicate proceeded from the periphery of the ejected mass towards the centre, the silica, under the influence of the volcanic agency, gradually penetrating to the interior of the calcareous spheroid.

5. *Allophane from Dehrn, near Limburg, in Nassau.*—This specimen consists of a principal stalactite, 8 centimeters long and about 4 thick,

to which are attached a number of smaller ones from 5 to 10 mm. long. It is perfectly transparent and colourless; has a strong lustre inclining to fatty; a conchoidal fracture; and is very brittle. The analysis of the mineral dried at 25° and ignited, gave the following results:—

	<i>Ignited.</i>	<i>Dried at 25°</i>
Silica .....	37.28	23.53
Alumina.....	59.76	37.73
Lime .....	3.05	1.92
Water.....	—	35.86
	<hr/> 100.09	<hr/> 100.04

Reckoning the small quantity of lime as silicate  $2\text{CaO} \cdot \text{SiO}_2$ , these numbers lead to the formula  $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  or  $\text{Al}_2\text{SiO}_5$  for the anhydrous, and  $\text{Al}_2\text{SiO}_5 \cdot 5\text{H}_2\text{O}$  for the hydrated mineral. About half the water is given off at 100°, nearly half the remainder by prolonged heating to 200°—220°; the rest at a red heat, but not quickly, except at the heat of a lamp urged by the blowpipe.

The specific gravity of the mineral in its natural state is 2.079; that of the ignited mineral 2.466.

6. *Composition of Babingtonite from Herbornseelbach in Nassau.*—This mineral, the crystalline form of which is described by vom Rath (*Pogg. Ann. Ergänzungsband*, v, 420), has been analysed by Dr. Jehn. The composition is given below, together with that of babingtonite from Arendal, analysed by Rammelsberg:—

	$\text{SiO}_2$	$\text{Fe}_2\text{O}_3$	$\text{FeO}$	$\text{MnO}$	$\text{CaO}$	$\text{MgO}$	Loss by ignition.
Herbornseelbach ..	50.44	17.01	7.49	3.22	19.90	1.45	0.43 = 99.94
Arendal .....	51.22	11.00	10.26	7.91	19.32	0.77	0.44 = 100.92

The amount of oxygen in the protoxides is to that in the sesquioxides in the Nassau mineral as 8 : 5; in the Arendal mineral as 3 : 1; but the ratio of the oxygen of the silica to that of all the bases together is in both minerals as 2 : 1.

7. *Euxenite.* This mineral, from the island of Hitteröe, near Flekkefjord in Lister, where other cerium and yttrium minerals (orthite, gadolinite, polycrase, ytterite) have long been found in the pegmatite veins lying upon the norite-gabbro, has also been analysed by Jehn. The mean of three of his analyses is given below, and compared with that of euxenite from Alve near Arendal, by Forbes and Dahll.

	$\text{Nb}_2\text{O}_5$	$\text{TiO}_2$	$\text{Al}_2\text{O}_3$	$\text{FeO}$	$\text{CaO}$	$\text{Ce}_2\text{O}_3$	$\text{YO}$	$\text{UO}$	$\text{MgO}$	$\text{H}_2\text{O}$
Hitteröe.	18.37	34.96	5.41	2.54	1.63	8.43	13.20	7.75	3.92	2.87 = 99.08
Alve....	32.58	14.36	3.12	1.98	1.37	3.31	29.36	5.22	0.19	2.88 = 100.37

Hence it appears that the composition of the euxenite of Hitteröe is totally different from that of Alve (as well as from that of euxenite from other localities). It is especially distinguished by the predominance of the titanic over the niobic acid, by the small quantity of yttria, and by the large proportion of uranous and ceric oxides.

H. W.

**Composition of the Gases evolved from the Mouths of the Solfatara of Puzzuoli.** By S. DE LUCA (*Compt. rend.*, lxxiv, 536—538).

THE emanations consist of carbonic acid, sulphuretted hydrogen, sulphurous acid, water vapour, compounds of iron and ammonia, and traces of arsenical matters. The arsenical matters can be detected ten meters from the point of emission. The gases from the principal mouth, taken at a depth of 3 meters, are perfectly free from atmospheric air.

J. B.

**Contributions to Micromineralogy.** By A. V. LASAULX (*Pogg. Ann.*, cxliv, 142—160).

POINTS out the great assistance afforded in the study of the petrographic constitution of rocks by the microscopic examination of thin sections, and describes the method of making the examination, illustrating it by several examples.

*The Microscopic Constitution of Clay-slates and Roofing Slates.*  
By F. ZIRKEL (*Pogg. Ann.*, cxliv, 319—329).

*Researches on the Compounds of Ilmenium and Niobium, and on the Composition of Niobium Minerals.* By R. HERMANN (*J. pr. Chem.* [2], iv, 178—211).

The following papers by G. vom Rath are crystallographic, and are copiously illustrated by figures:—

*On Humite Crystals from Nya Kopparberg, in Sweden* (*Pogg. Ann.*, cxliv, 563—576).—*Occurrence of Gadolinite in the Radauthal, Harz* (*ibid.*, 576—580).—*A new Twin-crystal of Zinc-oxide* (*ibid.*, 580—582).—*Iron Pyrites from Chichiliane, Dept. of Isère* (*ibid.*, 582—586).—*Blödite (Simonyite) from Stasfurt* (*ibid.*, 586—593).—*Perowskite, from the Wildkreuzjoch, between the Pfitsch and Pfunder valleys* (*ibid.*, 595).



## Organic Chemistry.

**On the Vapour-densities of certain Organic Compounds of High Boiling Point.** By C. GRAEBE (Deut. Chem. Ges. Ber., v, 15).

DEVILLE and Troost's apparatus was employed, about two grammes of substance being used, in glass bulbs holding 140—160 ccs., and heated in sulphur vapour; the substance remaining after each determination was examined to see if any decomposition had taken place:—

Substance.	Calculated.	Found.	Remarks.
Anthraquinone . . . .	$C_{14}H_8O_2 = 7.20$	7.33	B.P. above that of mercury.
Pyrene. . . . .	$C_{16}H_{10} = 7.0$	7.2	
Acenaphthene . . . .	$C_{12}H_{10} = 5.33$	5.35	Melted at 99°—100°.
Phthalic anhydride.	$C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} O = 5.12$	5.32	B.P. 277° C.
Acridine . . . . .	$C_{12}H_9N = 5.85$	$\left\{ \begin{array}{l} 6.10 \\ 6.3 \end{array} \right.$	$\left\{ \begin{array}{l} \text{Perfectly pure material.} \\ \text{Imperfectly pure material.} \end{array} \right.$

Chrysene and succinic anhydride are decomposed at the temperature of boiling sulphur. The hydrochloride of acridine is  $(C_{12}H_9N)_2 \cdot HCl$ , and by addition of hydrogen the base forms hydroacridine,  $C_{24}H_{20}N_2$ , which facts indicate  $C_{24}H_{18}N_2$  as the formula for acridine. Hydroacridine is not volatile without decomposition.

C. R. A. W.

**Derivatives of Lepidene.** By N. ZININ (Zeitschr. f. Chem. [2], vii, 483—484).

*Oxylepidene*,  $C_{28}H_{20}O_2$ , which is readily formed by treating a solution of lepidene in acetic acid with nitric acid or chromic acid, is easily further acted upon by chromic acid, *dioxylepidene*,  $C_{28}H_{20}O_3$ , being formed, which crystallises from alcohol in large rhombic, nearly quadratic plates. By the further action of chromic acid it yields benzoic acid and benzil, but reducing agents do not act upon it. When treated with a weak alcoholic solution of potash, it yields benzoic acid and desoxybenzoin, from which it appears that its rational formula is  $C_{14}H_{10}(C_7H_5O)_2O$ .

C. S.

**Oxidation of Tertiary Alcohols.** By A. BUTLEROW (Zeitschr. f. Chem. [2], vii, 484—486).

THE oxidation of tertiary alcohols takes place according to a law similar to that which rules the oxidation of ketones, the most simple alcohol radical remaining combined with the carbon-atom by which the whole group is kept together; whilst the two other radicals are oxidised

separately. The only exception to this rule appeared to be made by trimethyl-carbinol, which, as Butlerow formerly found, yielded acetone, acetic acid, and propionic acid. But on studying the oxidation-products of this alcohol more closely, he now finds that they consist chiefly of *acetone* (being an intermediate product) and *acetic acid*, besides a smaller quantity of *isobutyric acid*. The formation of this latter compound is not in contradiction to the above law; it is formed by a molecular change, corresponding to that by which Linne-mann has found that derivatives of trimethyl-carbinol are obtained from isobutyl alcohol.

C. S.

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**Action of Chlorine upon Isopropyl Chloride.** By F. FRIEDEL and R. D. SILVA (*Zeitschr. f. Chem.* [2], vii, 489—490).

By heating isopropyl iodide with an excess of mercuric chloride in closed vessels in a water-bath, very pure isopropyl chloride, boiling at 36°, is obtained. On acting on it with chlorine in the sunlight, two isomeric substitution-products are formed: the one boiling at 90° is *methyl-chloracetol*, yielding, when heated with silver benzoate, the characteristic benzoic ether, which forms fine clinorhombic octohedrons. The second product, which is always formed in smaller quantities (about one-fifth to two-thirds of the former), is *propylene dichloride*, boiling at 96°. It is not acted upon by silver benzoate, whilst the bromide, which was obtained by acting with bromine upon isopropyl iodide, as well as upon pure propylene, easily yields propylene benzoate as a thick sticky liquid, boiling at 240° under a pressure of 12—14 mm. of mercury. According to Meyer (*Compt. rend.*, lix, 444), this ether is crystalline and isomorphous with ethylene-benzoate; but Meyer's compound was most probably only the latter substance, the propylene which he obtained from amyl alcohol containing some ethylene. By heating isopropyl chloride with pure iodine monochloride to 120°, only propylene dichloride is formed, but no methyl-chloracetol.

C. S.

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**Presence of Pyrocatechin in Kino.** By F. A. FLÜCKIGER (*Deut. Chem. Ges. Ber.*, v, 1—4).

THE author contends that pyrocatechin is contained in the sap of the plants from which kino is prepared, and that it is not formed during its preparation, which simply consists in boiling down the sap, since the temperature at which this operation takes place cannot greatly exceed 100°. The residues from the ethereal extract of kino-gums from various sources, dissolved in water, gave in all cases the characteristic pyrocatechin reaction, viz., a grass-green coloration on the addition of ferric chloride, converted into red by lime-water.

H. E. A.

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**Contributions to the History of Orcin. No. II. Chlorine and Bromine Substitution-Compounds of the Orcins.** By J. STENHOUSE (*Proc. Roy. Soc.*, xx, 72—80).

THE author, after noticing what has been already published on this subject, proceeds to describe the methods for the preparation of *pentachlororcin*,  $C_7H_3Cl_5O_2$ . This substance is formed when a solution of orcin is added to a pulpy mixture of chlorine hydrate and water, or to a mixture of potassium chlorate and hydrochloric acid, always taking care to keep the chlorinating mixture in excess. The crude product is then purified by crystallisation from carbon disulphide. It forms large colourless prisms, which melt at  $120\cdot5^\circ$ . It is moderately soluble in carbon disulphide and benzol, readily in ether. It is but very slightly soluble in water, to which, however, it communicates an exceedingly disagreeable and persistent bitter metallic flavour. It appears to suffer decomposition when boiled either with alcohol or with water, trichlororcin being one of the products formed in the latter case.

*Trichlororcin*,  $C_7H_5Cl_3O_2$ .—This is readily obtained by the reduction of pure pentachlororcin with hydriodic acid and amorphous phosphorus. It is moderately soluble in boiling water, and crystallises out on cooling in colourless transparent needles, which melt at  $123^\circ$ . It is but sparingly soluble in carbon disulphide, moderately in petroleum oil and benzol, and excessively soluble in ether and alcohol. It dissolves in hot glacial acetic acid, from which it crystallises in thin transparent plates that become white and opaque on the addition of water. Heated to  $180^\circ$  with hydriodic acid and phosphorus it is reconverted into orcin.

*Pentabromorcin*,  $C_7H_3Br_5O_2$ , is easily prepared by adding an aqueous solution of orcin, with constant agitation, to a mixture of bromine and water, taking care that the bromine should be in slight excess. Its solution in carbon disulphide, in which it is moderately soluble, yields very large and almost colourless transparent crystals, melting at  $126^\circ$ . It is almost insoluble in water, very soluble in alcohol and ether, and moderately so in benzol. Pentabromorcin, when boiled with phosphorus and strong hydriodic acid, passes into solution, probably as orcin; but with very weak hydriodic acid, tribromorcin is formed, identical with that described by Stenhouse (*Phil. Trans.*, 1848, 87), and subsequently examined by Laurent and Gerhardt (*Ann. Chim. Phys.* [3], xxiv, 317), and by Lamparter (*Ann. Chem. Pharm.*, cxxxiv, 257).

*Pentachlororcin hypochlorite*,  $C_7H_4Cl_6O_3 = C_7H_3Cl_5O_2 \cdot HClO$ . When orcin is treated with hydrochloric acid and a solution of calcium hypochlorite, the two latter being in excess, a turbid solution is obtained, which, after the lapse of 24 hours, deposits white crystals. These, when crystallised from benzol, form colourless transparent prisms of great dispersive power, which melt at  $140\cdot5^\circ$ . The new compound is very soluble in ether, but, unlike pentachlororcin, only sparingly soluble in carbon disulphide. Treated with hydriodic acid and phosphorus it is decomposed, but the product has not yet been examined.

*Chlororesorcin*,  $C_6HCl_5O_2$ , is obtained, like the corresponding orcin



compound, by the action of hydrochloric acid and potassium chlorate on resorcin, and may be purified by crystallisation from carbon disulphide. The action of chlorine hydrate on resorcin gives unsatisfactory results. Anhydrous pentachlororesorcin is readily soluble in carbon disulphide, benzol, and petroleum naphtha, and very soluble in alcohol and ether. It melts at  $92.5^{\circ}$ , and is moderately soluble in warm water, from which it separates, on cooling, in a white opaque mass of indistinct crystals, apparently a hydrate. *Pentabromoresorcin*,  $C_6HBr_5O_2$ , is prepared like the corresponding orcin compound. It melts at  $113.5^{\circ}$ , and is almost insoluble in water, readily soluble in ether and alcohol, and moderately so in cold benzol. No resorcin compound corresponding to the pentachlororcin hypochlorite was obtained.

In conclusion, the author remarks that the view of the constitution of the orcins put forth by Kekulé, who regards them as dihydroxyl derivatives of the benzenes, is scarcely in accordance with the method of formation and composition of the compounds  $C_6HCl_5O_2$  and  $C_6HBr_5O_2$ , in the latter of which five hydrogen atoms in the resorcin are undoubtedly directly replaced by bromine, although one of them, according to Kekulé's view, should exist as hydroxyl.

C. E. G.

**Note on Fucosol.** By J. STENHOUSE (Proc. Roy. Soc., xx, 80—82).

WHEN seaweeds are boiled with dilute sulphuric acid (3 per cent.), a substance is obtained corresponding to that extracted from bran in a similar manner by Gudkow (*Zeitschr. f. Chem.*, 1870, 360). This, when distilled with sulphuric or hydrochloric acid, yields fucosol. The author has repeated, with great care, his examination of the difference in the physical properties of furfural and fucosol, and also the difference between the products obtained by the action of ammonia upon them and the bases derived from these, and finds his former statements (*Phil. Trans.* 1850, 467) to be correct. He has also prepared fucusaniline hydrochloride, which, like the corresponding furfuraniline salt (*Proc. Roy. Soc.*, xviii, 537) crystallises in needles of a magnificent purple colour. As it is well known that when furfural is boiled with water and silver oxide it yields argentic pyromucate,  $C_5H_3AgO_3$ , the author submitted fucosol to the same treatment. In this case a silver salt of a new acid,  $\beta$ -pyromucic acid, is formed, closely resembling pyromucic acid. The silver salt,  $C_5H_3AgO_3$ , is moderately soluble in boiling water, and crystallises on cooling in long flat needles, whilst ordinary argentic pyromucate forms small crystalline scales. The acid itself,  $C_5H_4O_3$ , separated from the silver salt by hydrochloric acid, crystallises from its aqueous solution in small rhomboidal plates melting at  $130^{\circ}$ , whilst ordinary  $\alpha$ -pyromucic acid forms flat needles whose melting point the author found to be  $133^{\circ}$ , and which Schwanert gives as  $134.3^{\circ}$ .

C. E. G.

**The Crystalline Principle of Aloes.** By F. A. FLÜCKIGER (Arch. Pharm. [2], cxlix, 11—21).

NATAL aloes, moistened with spirit and submitted to microscopical examination, exhibits the presence of crystals of a compound which is but slightly soluble in alcohol, so that, on treating the aloes with its own weight of that solvent at 120° F., the crystalline principle, which the author calls nataloïn, is readily obtained in a crude state. When purified by crystallisation from hot spirit, it forms thin, bright yellow scales, sparingly soluble in water, benzol, carbon disulphide, chloroform, and ether. Nataloïn,  $C_{34}H_{38}O_{15}$ , contains no water of crystallisation; it melts between 356° and 374·5° F., dissolves in concentrated sulphuric acid, and the addition of a crystal of potassium nitrate to this solution produces a characteristic bright green coloration, rapidly passing through red to blue. Heated with nitric acid it is decomposed, yielding oxalic acid without a trace of picric or chrysammic acid, thus showing a remarkable difference from aloïn. The author was unsuccessful in his attempts to obtain a bromine substitution-compound; neither did the action of dilute sulphuric acid or that of zinc and acetic acid on the compound give any satisfactory results. By washing Zanzibar aloes slightly with dilute spirit, the author has obtained crude Zanzibar aloïn, which, when purified by crystallisation from spirit, formed tufts of needles. It is far more soluble than nataloïn, and contains water of crystallisation,  $C_{34}H_{38}O_{15} + 5H_2O$ , which it loses when dried over sulphuric acid, leaving anhydrous Zanzibar aloïn,  $C_{34}H_{38}O_{15}$ , isomeric with the crystalline hydrated aloïn of Stenhouse. As the author has not succeeded in obtaining a bromine substitution-compound from it, and as it does not give the deep red colour with nitric acid which ordinary aloïn from Barbadoes aloes does, he considers it possible that it may be different from the latter.

C. E. G.

**Crystalline Substance from Alcornoco Bark.** By H. SPIRGATIS (N. Rep. Pharm., xx, 764).

AN indifferent substance, probably an alcohol, analogous to cholesterin, perhaps identical with the alcornin of Bilz.

**Iodide of Starch.** By E. DUCLAUX (Compt. rend., lxxiv, 533).

AN aqueous solution of starch is acted upon by iodine only when the water present contains a certain quantity of the latter in the free state. This quantity increases with the temperature, and this explains the decoloration by heat of iodide of starch formed in the cold. The state of equilibrium between the iodine, starch, and water is also modified by time. Iodide of starch has therefore no constant composition, and the irregularity of its formation renders many precautions necessary when it is used in volumetric analysis.

J. B.

**Cinnamic Acid.** By F. BEILSTEIN and A. KÜHLBERG  
(Zeitschr. f. Chem. [2], vii, 487—489).

CRUDE cinnamic acid prepared from styrax always contains, a resin and sometimes benzoic acid. To purify it, water and solid ammonium carbonate are added, and the mixture is allowed to stand for some time, being well stirred up. The solution is precipitated with hydrochloric acid, and the dried precipitate is distilled. First benzoic acid volatilises, and afterwards (between 280°—290°) cinnamic acid, which, in order to remove an oily substance adhering to it, is either pressed between filter paper or recrystallised from alcohol.

*Nitro-hydrocinnamic acid*, which, according to Glaser and Buchanan, softens on heating, and becomes perfectly liquid at 153°, is a mixture of two isomerides, of which the para-acid can be easily obtained in the pure state by recrystallisation from water, being less soluble than the other nitro-acid. It forms small flat needles, melting at 163°—164°. The barium salt of the crude acid forms a semi-liquid mass, whilst that of the pure acid crystallises in microscopic needles, containing, like the similar calcium salt, 2 mol. of water. The ether,  $C_6H_5(NO_2)(C_2H_5)O_2$ , forms long flat crystals melting at 33°—34°. On oxidising para-nitrocinnamic acid, it yields para-nitrobenzoic acid.

As it was to be expected, cinnamic acid also yields two isomeric nitro-acids. To obtain these, it is not necessary to use a pure nitric acid, as it is stated, but fuming acid will do as well. The para-acid can easily be obtained perfectly pure, as it is very sparingly soluble in alcohol. It forms fine needles, melting at 265° (according to former observers at about 270°). The second isomeric modification is much more soluble in alcohol, and was mistaken by former observers as being a mixture of benzoic acid, nitrobenzoic acid, and other oxidation products of cinnamic acid.

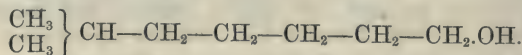
By dissolving para-nitrocinnamic acid in a solution of soda crystals and passing chlorine into the liquid,  $\beta$ -nitrophenyl-chlorolactic acid,  $C_6H_5(NO_2)ClO_3$  is formed, which melts at 166°, and is more sparingly soluble in water and a more stable compound than chlorphenyl-lactic acid.

C. S.

**Nonylic Acid from the Octyl Alcohol of Heracleum Oil.**

By A. FRANCHIMONT and TH. ZINCKE (Deut. Chem. Ges. Ber., v, 19).

THE octyl alcohol of the exotic heracleum oil contains the butyric ether of normal hexyl alcohol (probably) and the acetic ether of an octyl alcohol, apparently identical with that derived from the indigenous plant, *i.e.*, having the formula—



This was converted into the iodide, the latter into the cyanide, and finally into the nonylic acid by heating with alcoholic potash and distillation with diluted sulphuric acid. This acid forms a colourless oily fluid of



weak odour, solidifying to a crystalline mass at low temperatures, and beginning to melt again at  $+10^{\circ}$ ; the acid from the recrystallised barium salt melts at  $12^{\circ}$ — $12.5^{\circ}$ , solidifies at  $+11.5^{\circ}$ , and gives the same numbers after distillation, solidification, and severe pressure. Its boiling point is  $253^{\circ}$ — $254^{\circ}$ , at 758.8 mm., and its sp. gr. 0.9065 at  $17.5$ . In water it is sparingly soluble, and it distils but slowly with aqueous vapour.

The methyl ether,  $C_9H_{17}O.OCH_3$ , is a colourless liquid of sp. gr. 0.8765 at  $17.5^{\circ}$  and boiling point  $213^{\circ}$ — $214^{\circ}$  at 756.83 mm.

The ethylic ether,  $C_9H_{17}O.OC_2H_5$ , has a sp. gr. 0.8655 at  $17.5^{\circ}$ , and boiling point  $227^{\circ}$ — $228^{\circ}$  at 756.92 mm.

The potassium, sodium, and ammonium salts form small pearly scales; the first is decomposed by hot alcohol, the last, on warming its aqueous solution. The barium, calcium, copper, cadmium, zinc, and lead salts were obtained in crystals from alcoholic solution; some of them are basic.

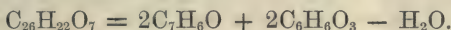
Experiments are contemplated on the pelargonic acid from oil of rue, to see if it is identical with this nonylic acid.

C. R. A. W.

### Compounds of the Aldehydes with the Phenols. By A. BÄYER (Deut. Chem. Ges. Ber., v, 25).

ORDINARY aldehyde when mixed with pyrogallie acid and hydrochloric acid, and gently warmed, produces a red coloration, becoming violet on the addition of an alkali.

Bitter almond-oil heated with pyrogallie acid, produces a colourless body, crystallisable from ether, and having the composition (dried at  $120^{\circ}$ )—



Heated to  $200^{\circ}$ , this product loses hydrogen, forming a red body, soluble in alcohol,  $C_{26}H_{16}O_7$ ; while on treating it with hydrochloric acid, alcohol, and zinc, hydrogen is added, and a crystalline white body, soluble in acetone, but insoluble in alcohol and ether is produced; the composition of this is  $C_{26}H_{24}O_7$ .

Resorcin behaves similarly with bitter almond-oil; and a phenol dye-stuff is produced on adding strong sulphuric acid to a mixture of phenol and bitter almond-oil.

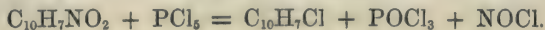
Aldehyde and phenol with sulphuric acid; chloral similarly treated; furfural and resorcin, phenol, or pyrogallie acid with a trace of hydrochloric acid; salicylic and pyrotartaric acids with phenols: all give colouring matters.

C. R. A. W.

### Action of Phosphorus Pentachloride on Nitronaphthalene.

By L. DE KONINCK and P. MARQUART (Deut. Chem. Ges. Ber., v, 11).

On heating together these substances, the following reaction takes place:—



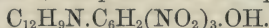
The resulting chloronaphthalene boils at  $251^{\circ}$ — $253^{\circ}$ , and has the sp. gr. 1.2025 at  $15^{\circ}$ . Neither nitrobenzene nor rhombic dinitronaphthalene is acted on by phosphorous pentachloride: the former is converted, by hydrobromic acid, into bromaniline, while nitronaphthalene exchanges its nitrogenous radical for bromine; so also phosphorus pentasulphide acts vigorously on nitronaphthalene, but has no action on nitrobenzene. Nitronaphthalene distils at  $304^{\circ}$ .

C. R. A. W.

**Carbazol.** By C. GRAEBE and C. GLASER (Dent. Chem. Ges. Ber., v, 12).

IN crude anthracene a substance occurs which forms a beautiful red crystalline compound with picric acid; it is insoluble in dilute acids and alkalis, and much resembles anthracene in appearance; it melts somewhat higher, namely, at  $238^{\circ}$ , and contains nitrogen, having the formula  $C_{12}H_9N$ . This substance, called carbazol, is insoluble in water, but soluble in ether, alcohol, and benzene, especially on warming; its boiling point is  $338^{\circ}$ ; its vapour-density in sulphur vapour is found to be 5.97, 5.96, and 6.01, instead of 5.85 (calculated); neither red-hot zinc-dust nor soda-lime, nor distillation through a red-hot tube has any action on it; with hot nitric or sulphuric acid, it forms mono- and di-nitrocarbazol, and carbazol-disulphonic acid respectively. Concentrated hydrochloric acid at  $250^{\circ}$ , alcoholic potash at above  $200^{\circ}$ , and fusion with caustic potash have no action upon it; hydriodic acid produces no change at  $200^{\circ}$ , but at higher temperatures a tarry carbonaceous product; in presence of phosphorus at  $200^{\circ}$ — $220^{\circ}$ , 6 atoms of hydrogen are taken up, *carbazoline*,  $C_{12}H_{15}N$ , being formed; sodium amalgam and water, however, are without action, even after several days; it does not form salts with acids.

Dissolved in glacial acetic acid, it is readily oxidised by chromic acid, but no well-marked body is produced; chlorine and bromine give substitution-products; its picric acid compound is—



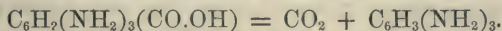
This is slightly soluble in cold benzene, readily in hot benzene or ether; water and alcohol decompose it. In all these properties carbazol resembles a hydrocarbon, such as anthracene, much more than a nitrogenous basic substance.

Carbazoline crystallises from alcohol in large white needles; it melts at  $96^{\circ}$ , and distils at  $286^{\circ}$  (uncorrected); its vapour-density is 6.13, 5.99 being the calculated density for  $C_{12}H_{15}N$ ; it sublimes in needles, and is volatile with water-vapour; it is readily soluble in alcohol, ether, and benzene, and forms salts with acids very soluble in water and alcohol; its hydrochloride is  $C_{12}H_{15}N.HCl$ . Platinic chloride, ferric chloride, potassium dichromate, and potassium permanganate, readily oxidise its solutions, even in the cold, with formation of a brown amorphous mass; nitric acid of sp. gr. 1.2, forms a resinous body; red-hot soda-lime and melting caustic potash are without action on it.

C. R. A. W.

**Triamidobenzene.** By H. SALKOWSKI (Deut. Chem. Ges. Ber., v, 22).

CHRYSANISIC acid (dinitro-amidobenzoic acid) forms triamidobenzoic acid on treatment with tin and hydrochloric acid; when the salts of this acid, or the acid itself mixed with ten times its weight of powdered glass are heated, the following reaction ensues:—



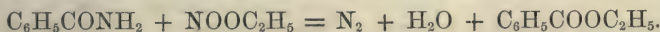
The triamidobenzene thus produced amounts to 71—75 per cent. of the theoretical yield, and is purified by distillation; it forms a solid, dark-red crystalline mass, melting in capillary tubes at 103°—104°, and distilling unchanged at about 300°; it is volatile even at 100°, with an odour recalling that of aniline, and is readily soluble in water, alcohol, and ether; the aqueous solution yields, with ferric chloride, a precipitate at first dark violet, then brown, and reduces ammoniacal silver solutions in the cold, more readily on warming. Its salts are crystalline, but only contain two equivalents of acid; the hydrochloride forms anhydrous needles,  $\text{C}_6\text{H}_3(\text{NH}_2)_3 \cdot 2\text{HCl}$ ; the sulphate forms crystalline plates,  $\text{C}_6\text{H}_3(\text{NH}_2)_3 \cdot \text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$ .

Researches are in progress in the endeavour to obtain the isomeric triamidobenzenes which should theoretically exist.

C. R. A. W.

**Note on the Action of Nitrous Ether on Benzamide.** By V. MEYER and O. STÜBER (Deut. Chem. Ges. Ber., iv, 962).

THE reaction is effected by heating for a short time in sealed tubes to about 120°; the products are—nitrogen, water, and ethylbenzoate:



H. E. A.

**Isomeric Dibromobenzenes and Dibromaniline.** By V. MEYER and O. STÜBER (Deut. Chem. Ges. Ber., iv, 956—961, and v, 52—56).

IT has been hitherto assumed that Riche and Bérard's (*Compt. rend.*, lix, 142) dibromaniline, obtained by reducing nitro-dibromobenzene—prepared by nitration of ordinary solid dibromobenzene—is identical with the dibromaniline from acetanilide. The authors show that this is not the case; they have prepared dibromaniline by agitating acetanilide suspended in water with 2 mols. of bromine, and decomposing the resulting dibromacetanilide with alcoholic potash; this dibromaniline they reduced to dibromobenzene by adding it to a nearly saturated alcoholic solution of nitrous acid (nitrous ether). Reaction commences in the cold, and is completed by warming; subsequent addition of water causes the separation of an oil of the composition  $\text{C}_6\text{H}_4\text{Br}_2$ .

This isomeric dibromobenzene, when pure, is a clear, colourless liquid, boiling at about 215°, and does not solidify, even at -28° (ordinary dibromobenzene is a magnificently crystalline body, which melts at



89°). With a view to determine its constitution, attempts were made to form from it a dimethylbenzene by treatment with methyl iodide and sodium, but unsuccessfully. It is not perceptibly acted on by the strongest nitric acid in the cold, but dissolves only on warming, and is converted into *nitrodibromobenzene*, which may be obtained in fine, glistening, pale-yellow, interlaced needles, melting at 60°—61°.

A *liquid* dibromobenzene, also boiling at about 215°, has been described by Riese (*Deut. Chem. Ges. Ber.*, ii, 61), who obtained it in small quantity, simultaneously with ordinary dibromobenzene, by the action of bromine on benzene. It differs slightly from the above, since (1) it may be solidified in a freezing mixture, melting again at -1°; (2) it dissolves *readily* in cold fuming nitric acid, with considerable evolution of heat, being converted into nitrodibromobenzene, melting at 58°. The authors have repeated Reise's experiments, and confirm his observations absolutely; so that there is no doubt that the above two dibromobenzenes are isomeric, though they differ to a slight extent. In external appearance, their nitro-derivatives are scarcely distinguishable.

Accordingly, there are now three known isomeric dibromobenzenes, the distinctive properties of which are evident from the following table:—

Dibromobenzenes.	Melting-point.	Boiling-point.	Behaviour with HNO <sub>3</sub> .	Mononitro-derivative.
Couper's 1 : 4...	89°	219°	Dissolved on warming.	Plates or flat needles. Melting point, 84°.
Riese's 1 : 2 (?) ..	- 1°	213°—215° (corrected: Riese).	Dissolved with spontaneous evolution of heat.	Fine needles. Melting-point, 58°.
V. Meyer and O. Stüber's 1 : 3 (?).	Liquid at -28°.	About 215° (uncorrected).	Dissolved on warming.	Needles. Melting-point, 60°—61°.

*Dibromaniline*.—Riche and Bérard gave no description of the properties of their dibromaniline; the authors have, therefore, prepared it by reduction of nitrodibromobenzene with tin and hydrochloric acid, and compared it with the dibromaniline from acetanilide.

The base,  $C_6H_3Br_2NH_2$ , forms well crystallised, but extremely unstable, salts; its tendency to unite with acids is very weak, so much so that a considerable portion often separates out in the free state from a strong hydrochloric acid solution. It is insoluble in water, but very soluble in alcohol, from which it crystallises in silky, glistening prisms, united in groups; the melting point is 60°—61° (dibromaniline from acetanilide melts at 79·5°). It usually separates from the concentrated alcoholic solution as an oil, which often remains liquid for hours; ordinary dibromaniline (from acetanilide) separates from a hot alcoholic solution, even when impure, at once in the crystalline form.

The nitrate, obtained by long digestion of the base with dilute acid, crystallises in magnificent glistening plates; it cannot be dissolved in water without undergoing partial decomposition into acid and base.

The authors attempted to convert  $\alpha$ -nitraniline and  $\alpha$ -nitroacetanilide by nitration into dinitroaniline, but unsuccessfully.  $\alpha$ -nitroacetanilide (from  $\alpha$ -nitraniline and acetyl chloride) crystallises in pale yellow, glistening plates, which melt at  $141^{\circ}$ — $143^{\circ}$  ( $\beta$ -nitroacetanilide, from acetanilide, melts at  $207^{\circ}$ ).

The non-identity of the two dibromanilines affords, in the opinion of the authors, further confirmation of the rule which one of them (V. Meyer) maintains to have proved in a previous paper (*Ann. Ch. Pharm.*, 156, 286), viz., that in the formation of Cl, Br, I and  $\text{NO}_2$  substitution-compounds from aromatic amines, the substituting groups replace the hydrogen united to the carbon-atom which is contiguous to that with which the  $\text{NH}_2$ -group is combined, or, in other words, that the  $\text{NH}_2$ -group exercises an attractive action on Cl, Br, &c. Considerations, into which they enter at length, arising from this rule led them to doubt the supposed identity of the two dibromanilines, and to institute the above experiments.

H. E. A.

**Tribromaniline.** By O. STÜBER (*Deut. Chem. Ges. Ber.*, iv, 961).

As bye-product in the preparation of dibromobenzene from dibromaniline as above, crystalline needles of a body melting at  $115^{\circ}$ , were obtained; the most probable assumption as to the nature of which appeared to be, that they consisted of a new tribromobenzene derived from traces of tribromaniline present in the dibromaniline.

This assumption has proved to be correct: the author has reduced tribromaniline (prepared by treating aniline hydrochloride with bromine) to tribromobenzene by the action of nitrous ether. Reaction commences in the cold, and is completed by warming; subsequently the cold solution deposits a quantity of long, brown needles, which, after purification by distillation, &c., are obtained in the form of fine, brilliant white needles, melting at  $118.5^{\circ}$ . This new tribromobenzene is difficultly soluble, even in boiling alcohol; it sublimes below  $100^{\circ}$  in broad needles. The tribromobenzene previously known melts at  $44^{\circ}$ .

H. E. A.

**The Aconite Alkaloids of Hübschmann, Napelline and Lycoctonine, and their Physiological Actions.** By C. v. SCHROFF, Jun. (*N. Repert. Pharm.*, xx, 641).

HÜBSCHMANN extracted from crude aconitine, obtained from *Aconitum Napellus*, an alkaloid, napelline, differing in its solubility in water from aconitine; and subsequently from lycoctonum-root two alkaloids, acolyctine and lycoctonine, the first of which he found to be identical with napelline. The author obtained these bases by treating the alcoholic tincture of the root with lime, then with sulphuric acid; evaporation of the alcohol, and solution of the residue in water, whereby resinous matters were separated; decolorisation with purified bone-charcoal; evaporation to dryness after addition of sodium carbonate to strongly alkaline reaction; exhaustion with alcohol; and

finally separation of the two bases by ether, in which lycoctonine is readily soluble, whereas acolyetine is insoluble.

Acolyetine thus obtained is a white powder soluble in water, alcohol, and chloroform, but insoluble in ether; it forms white precipitates with tannin and lead acetate, and yellow with gold chloride; its sulphate precipitates white with ammonium molybdate. Lycoctonine forms white prisms and crystalline needles of intensely bitter taste, soluble in alcohol, chloroform ether, benzol, amylic alcohol, petroleum spirit, oil of almonds, and oil of turpentine; only sparingly soluble in water (1 part in 800 at 17°); its aqueous solution gives a yellow precipitate of microscopic needles with bromine-water, and a thick precipitate becoming crystalline on standing with potassium-mercury-iodide.

A large number of physiological experiments were made on men, rabbits, and frogs, with these results: acolyetine is not identical with napelline, but has only about one-third as energetic an action; lycoctonine is about as energetic as acolyetine, the action of each being analogous to that of aconitine. No analytical numbers are given in the paper.

Further experiments are given in a subsequent paper by the author, entitled "On the Active Ingredients of *Aconitum Lycortonum*, on *Aconitum Napellus*, and *Morson's Aconitine* (Pseudaconitine)." (N. Repert. Pharm., xx, 705.)

C. R. A. W.

### On Leucoline Oil and the Pure Naphthalene of Commerce.

By M. BALLO (Dingl. Polyt. f., ccii, 377—380).

THE strong tarry odour of pure commercial naphthalene is for the most part due to the presence of impurity, the really pure substance possessing a faint and not unpleasant odour.

A quantity of the crude naphthalene, which had never been treated with acids and alkalis, was boiled on the water-bath, and the brown solution obtained was precipitated with ammonia. A flocculent precipitate was formed, which on drying at a higher temperature or *in vacuo* over sulphuric acid, always fused to a dark thick fluid, possessing in an eminent degree the characteristic odour of impure naphthalene. Potassium bichromate produced also very bulky precipitates, which dried up to brown hard masses, but the precipitation was not complete. The oily liquid obtained as above was distilled, a light brownish yellow coloured distillate coming over; it was then further purified by fractional distillation, the portion coming over at 240° being collected. The distillate was not fully soluble in hydrochloric acid. By shaking with dilute hydrochloric acid, pouring off from the indifferent oils, and then adding ammonia to the solution, the oily body was precipitated in a milky form, gradually collecting in drops at the bottom of the vessel. This oily layer was completely soluble in hydrochloric acid. Dried *in vacuo*, it was quite clear, but became somewhat dark coloured. To this body the author gives the name of *leucoline oil*. This oil appearing to be a mixture of several bases, the author endeavoured to effect a separation of them by obtaining their salts, but he failed to obtain



any crystalline body. The sulphate is precipitated from the ethereal solution of the oil, after addition of a few drops of dilute sulphuric acid, in the form of a yellowish brown oil, and in the strongly acid aqueous solution of the sulphate, potassium bichromate produces a bulky yellow precipitate. Red litmus paper is not turned blue by the oil, and it produces grease stains on blotting paper. These properties lead the author to the belief that the oil contains leucoline. Platinic chloride yields in a solution of leucoline oil in dilute hydrochloric acid a yellow precipitate; in the filtrate, after standing some days, further portions crystallise out in long feathery groups of orange-yellow needles. These dried *in vacuo* over sulphuric acid, and then at  $100^{\circ}$ , gave on analysis 28.03 p.c. of platinum;  $(C_{10}H_9NHCl)_2PtCl_4$  contains 28.3 p.c. Pt. The first formed precipitate was treated with alcohol in excess, but was not all dissolved; the undissolved portion contained 29.2 p.c. Pt, and the recrystallised portion 29.7 p.c.

The oil therefore appears to be a mixture of leucoline and lepidine. The platinum salt of the first-named contains 29.3 p.c. Pt. The leucoline oil by treatment with amyl-iodide and potassium hydrate solution gives a violet colouring matter, apparently identical with that obtained from cinchonine-chinoline, and practically contradicts C. Greville Williams' assertion that coal tar leucoline gives no colour.

W. S.

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## Physiological Chemistry.

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**The Oxidation-products of Bile-Pigments and their Absorption-bands.** By A. HEYNSIUS and J. F. F. CAMPBELL (Pflüger's Arch. f. Physiol., iv, 497—547).

THE greater part of this paper is taken up with a very copious account of the previous labours of Berzelius, Heintz, Jaffé, Stokvis, Städeler, Fudakowsky, Bogornoloff, Maly, and others, on the bile-pigments, their mutual relations, and their absorption-spectra. This is followed by an elaborate account, illustrated by a plate, of the various spectra exhibited by bile and by bile-pigments when treated with oxidising agents. Lastly, there is a description of bilicyanin (Stokvis's choleverdin), and of Maly's choletelin, two bodies obtained respectively by a moderate and a more complete oxidation of bilirubin and other bile-pigments.

Bilicyanin was obtained from bilirubin by the oxidation of this substance with bromine-water. No elementary analysis was made, and it is obvious that the product was impure, the spectra being variable, and its solubility not constant. It gives two or perhaps three absorption-bands in the yellow and green.

Choletelin was procured from bilirubin and bilihumin by oxidising these in alcoholic solution with nitrous vapours. It does not give Gmelin's reaction for bile-pigment. The substance was perhaps impure, no elementary analysis being made; but the spectrum was more constant than that of bilicyanin, consisting of one broad absorption-band

extending from a little beyond *b* to F when in acid solution; in an alkaline solution the band is rather less refrangible.

The authors state that bilicyanin is not a normal constituent of bile-pigment till after oxidation by exposure to the air or other means; that it is a constituent of gall-stones; and that though they were unable to detect it in urine it may be present therein. Since this pigment reacts somewhat like indican with hydrochloric acid, the presence of bilicyanin in urine may have been mistaken for indican.

Choletelin was often found by its spectroscopic appearances in icteric, but never in normal urine. None was detected in gall-stones. The fact that choletelin does not yield Gmelin's reaction for bile-pigment accounts for the observation that certain dark urines in jaundice fail to give Gmelin's reaction.

The spectrum yielded by the violet-red liquid obtained on performing Pettenkofer's test with sodium glycocholate, is described. It consists of three bands, one extending from midway betwixt C and D to D, a second midway between D and E, and the third between *b* and F.

T. S.

### A Reducible By-product of the Oxidation of Bile Pigment.

By B. J. STOKVIS (N. Rep. Pharm., xxi, 123).

IN most cases of oxidation of the bile colouring matter which gives Gmelin's reaction, a reducible by-product is formed. The substance is colourless, or of a light yellow tint, and is soluble in water, alcohol, and dilute acids. It becomes of a beautiful rose-red colour when boiled with reducing agents in alkaline solutions. The red solution gives in the spectrum a tolerably broad absorption-band in the green. In concentrated solutions (thick strata) the band begins close on the line D, and extends to *b*. In dilute solutions (thin strata) it occupies only two-thirds of the interspace between D and E, ending short of E. Shaking with air causes both the rose colour and the absorption-band to disappear. This by-product differs from the bile colouring matter and other oxidation-products of the same in being insoluble in chloroform and ether, and in not forming insoluble compounds with neutral or basic lead acetate. With ammonia and basic lead acetate it is precipitated.

This substance exists as such in the gall-stones both of man and of the ox. It can be obtained from them by simple boiling with distilled water, and extraction with dilute acids. It does not exist in fresh bile. It occurs in the urine of animals which have been starved for some days previously, in icteric urine, and in the urine of febrile diseases, such as small-pox, typhus, &c. It is not found in healthy urine. It seems to be present in the alimentary canal, although in direct experiments with different kinds of food little or none could be found.

In alkaline solutions the substance soon loses its characteristic properties. The occurrence of this substance in any liquid of neutral or acid reaction indicates not merely that oxidation of bile colouring matter has taken place, but also more generally that bile pigments have been present. It is, therefore, a delicate test for these substances. In applying the test, the liquid is to be precipitated with lead acetate, excess

of lead to be removed by oxalic acid, and the filtrate concentrated and boiled with alkalis and some reducing agent. If no reduction takes place, and if the other tests for bile colouring matter have given a negative result, the absence of this substance is proved beyond a doubt.

D. F.

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**Animal Cellulose.** By Dr. SCHÄFER (Ann. Chem. Pharm., clx, 312—329).

DR. SCHÄFER, from his analyses of the mantles of specimens of the *Pyrosomidae*, *Salpidae*, and *Phallusia mamillaris*, finds that the cellulose, or tunicin (Berthelot), derived from them has a complete identity with vegetable cellulose. The mantles, after being boiled in a Papin's digester, to remove chondrigen (see next abstract), were treated with dilute hydrochloric acid to remove the inorganic constituents. These consisted of calcium sulphate, sodium sulphate, and traces of iron, calcium carbonate, and calcium phosphate. The mantles were then boiled for several days in a saturated solution of caustic potash, and subsequently washed with alcohol and water. The mantles so heated retained their original form, but had become quite transparent like glass, but not horny, as Berthelot found in *Cynthia papillata*. The substance is quite free from nitrogen. The percentage composition is carbon 44.09, hydrogen 6.30, oxygen 49.61.

With iodine and sulphuric acid it gives a violet colour like vegetable cellulose. An important reaction is its solubility in ammonio-cupric oxide, from which it is precipitated like cellulose by acids. The precipitate is soluble in dilute hydrochloric acid, and gives the cellulose reaction with iodine and zinc chloride. It is converted into sugar by prolonged heating with dilute sulphuric acid in closed tubes. Like vegetable cellulose, it is converted into pyroxylin by the action of fuming nitric acid. The mantles so converted into pyroxylin retain their form, but are very brittle. They are soluble in ether, which on evaporation leaves a film like the ordinary collodion film.

These reactions leave little doubt of the complete identity of animal and vegetable cellulose.

D. F.

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**Occurrence of Chondrigen in the Tunicata.** By Dr. SCHÄFER (Ann. Chem. Pharm., clx, 330—333).

DR. SCHÄFER, at the suggestion of Dr. Hilger, who had found chondrigen in the *Brachiopoda* and *Holothuridae*, investigated its occurrence in the tunicata. By boiling the mantles for some time in a Papin's digester, an opalescent solution was obtained, which, however, could not be got to gelatinise. It was precipitated by acetic acid, insoluble in excess, by basic and neutral lead acetate, and voluminously by alum. Tannin caused no turbidity or precipitate. To avoid error from the presence of substances used in precipitating it, the nitrogen amount was determined from the residue left on evaporation of the watery solution after treatment with dilute hydrochloric acid, and washing



with alcohol and water. The amount found was 14.99 per cent., which agrees essentially with that of chondrin as given by Scherer, Mulder, and Vogel. A more complete elementary analysis was impossible from deficiency of material.

D. F.

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**Occurrence of Paralbumin in Serous Transudates.** By  
DR. HILGER (Ann. Chem. Pharm., clx, 338).

IN two cases of ascites fluid Dr. Hilger has found an albuminoid substance characterised by its solubility in water after precipitation by alcohol, and also by its incomplete coagulation by small quantities of acetic acid. This substance—paralbumin—has hitherto been found only in ovarian cysts.

D. F.

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**Influence of Alcohol on the Temperature of Healthy Men.**  
By C. BINZ (N. Repert. Pharm., xxi, 116—122).

THE old idea that alcoholic drinks heighten the temperature of the body has received numerous contradictions in recent times. Experiments on mammals in Binz's laboratory have shown that alcohol causes a transient though distinct diminution of the temperature when given in doses not at all destructive to the life of the animal.

The difficulties in determining the question with exactness in the case of man are great, partly owing to the fact of alcohol being used as an ordinary article of food, and partly on the difficulty of carrying out accurate observations. Binz communicates the results of experiments performed by Dr. Mainzer on himself and on another healthy individual of strong constitution. The observations were carried out with great care and avoidance of all conceivable sources of fallacy. Mainzer, in making observations on himself during the day, lay in bed lightly covered, and determined the temperature by means of a Geissler's thermometer in the rectum, which was read off every fifteen minutes. The normal curve was previously determined for the hours at which alcohol was taken, namely, between 7–10 in the morning, 3–7 afternoon, and 9–12 in the evening. The alcohol taken was alcohol of 98 per cent., diluted with twice or thrice its bulk of water. The quantities taken were 15, 40, 50, 75, and 80 cub. cent. Tables are given of the normal and alcohol curves obtained. As the result of his observations Mainzer concludes that there is no appreciable alteration in the temperature when alcohol is taken in doses of from 15–80 cubic centimeters.

The other individual experimented on seemed slightly more sensitive to the action of alcohol, and there was exhibited a slight tendency to a fall in temperature, varying from  $0.4^{\circ}$ – $0.3^{\circ}$  on an average. In regard to the action of alcohol on the temperature in pathological conditions, there are various views. The method adopted by Mainzer seems likely to lead to satisfactory results in these cases also.

D. F.

**On the Mucous Tissue of the Umbilical Cord.** By S. OBOLENSKY. (Pflüger's Archiv., iv, 349).

THE mucous tissue of the human umbilical cord, freed from vessels, cut into small pieces, and extracted with cold water, yields a solution which gives with acetic acid a precipitate soluble in excess. With alcohol it gives a precipitate which, when heated with dilute sulphuric acid over a boiling water-bath for some time, yields a substance which does not ferment, but reduces oxide of copper or bismuth, and is the same as that obtained by a like treatment of mucin.

It is probable that the amount of mucin in the umbilical cord cannot be directly determined by acetic acid, on account of the albuminous substances which are extracted along with it, but that the copper reducing body is yielded by it. It is possible that there may be different kinds of mucin, which all yield it.

T. L. B.

**On the Tension of the Gases of the Blood in the Pulmonary Capillaries.** By SIEGFRIED WOLFFBERG (Pflüger's Archiv., iv, 465—492).

THE author considers that experiments on the tension of the gases in the blood, made by shaking it with air of ascertained composition, are not to be relied on, as a diminution of the alkalinity of the blood has been shown to take place after it has been withdrawn from the body, and the tension thus becomes altered. The tension must, therefore, be determined while the blood is still in the vessels. Ludwig and Becher's plan of holding the breath as long as possible, so that the tension of the gases in the blood and lungs may be equalised, and then analysing the expired air, does not give the normal tension of the gases in venous blood, as it becomes overloaded with carbonic acid in consequence of the stoppage of respiration. In order to avoid this error the author, under Pflüger's direction, experimented on the air from one lobe of a lung only, so that the respiration was not much interfered with. He did this by passing into the lung of a dog, through a tracheal fistula, a catheter, which was surrounded at its lower end by a small india-rubber bag, which could be inflated at will, so as to make it fit the bronchus tightly, and completely prevent the entrance or exit of air from the lung beyond it. The tension of the gases in the blood and lung became equal in 3—4 minutes. The mean tension of the oxygen in the pulmonary capillaries is equal to 27 millimeters of mercury. As the tension of the oxygen in blood increases with its saturation with it, the tension of oxygen in arterial blood is probably not less than 9 centimetres of mercury. The tension of the carbonic acid is 24 millimeters (3·2 per cent.  $\text{CO}_2$ ). This low tension might be partly due to tracheotomy, and to the warmth of the weather when the experiment was made.

The maximum observed was 4·2 per cent.

The air expired from the lungs of a dog in ordinary respiration contained on an average 2·8 per cent.  $\text{CO}_2$  and 16·6 per cent. of oxygen.

In order to ascertain the tension of the carbonic acid in the blood of the right ventricle and pulmonary artery, he shook it before coagulation with air containing a definite amount of carbonic acid, and found that the tension of the carbonic acid in the blood was equal to that in an atmosphere containing 3·6 to 5·1 per cent. carbonic acid, sometimes slightly exceeding these limits.

He concludes that there is no ground for believing that the lung has a specific power of excreting carbonic acid, and thinks that such an apparent power is due to the death of the lung, and formation of acid during its death. Confirming this view he found that when the pulmonary vessels were washed out with salt-solution immediately after death, and then filled with a  $\frac{1}{4}$  per cent. solution of sodium carbonate, and allowed to stand at blood heat, the air in the lungs which had been previously compressed and filled with pure air, contained, after standing for an hour and a quarter at blood heat, air with 1·3 per cent.  $\text{CO}_2$ .

For his other arguments against Müller's conclusion, as well as for the details of his method of experimenting, I must refer to the original.

T. L. B.

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**Influence of Acids upon the Oxygen of Hæmoglobin.** By  
GUSTAV STRASSBURG (Pflüger's Archiv., iv, 454—461).

PFLÜGER and Zuntz confirmed Lothar Meyer's observation that the addition of tartaric acid to the blood caused a large proportion of the oxygen it contained to disappear. They also found that phosphoric acid has a similar action, and believed it to be due to the hæmoglobin being split up by the acid, and one of the products of its decomposition becoming afterwards oxidized at the expense of the oxygen in the blood. Strassburg, under Pflüger's direction, continued these experiments, and found that the addition of phosphoric acid to chemically pure hæmoglobin suspended in water or dissolved in sodium carbonate, caused oxygen to disappear from it in the same manner as from blood, thus confirming Pflüger's theory. He finds the amount of oxygen which is loosely combined with dry hæmoglobin at  $0^\circ$ , and one meter pressure, to be from 0·4483 to 0·8852, instead of 1·277 c.c., as found by Preyer. From the inconstant amount which he obtained, he is of opinion that oxidation takes place in solutions of hæmoglobin saturated with oxygen, and that part of the oxygen consequently disappears during the process of pumping out the blood gases.

T. L. B.

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**Influence of Cutaneous Irritation on Tissue Change.** By  
F. PAALZOW (Pflüger's Archiv., iv, 492—496).

THE experiments of Röhrig and Zuntz had rendered it probable that all irritations applied to the skin exercise a great influence on tissue change in the body, and as carbonic acid baths are recommended as stimulants to the skin, Paalzow tested the action of water saturated



with carbonic acid on rabbits, but found that it neither increased the amount of oxygen and carbonic acid expired by rabbits, nor did it redden the skin either in them or in man. He thinks the effect of carbonic acid baths which has been ascribed to the carbonic acid dissolved in the water, is really due to alkaline salts. On applying real irritants, such as mustard, to the skin of rabbits, he found the consumption of oxygen and the production of carbonic acid invariably increased, often by more than one-half, *i.e.*, tissue change in the body was rendered much more rapid by the application of the irritant. The relation between the oxygen consumed and the carbonic acid evolved, was not constant. The quotient  $\frac{\text{CO}_2}{\text{O}}$  often greatly exceeded unity,

while at other times it was under it, as it usually was before the irritant was applied. There were no muscular movements of the animal at all sufficient to explain this increased tissue change. Nor could it be due to cooling of the animal during the operation, for it was kept carefully covered, and a thermometer in the rectum never varied more than  $0.3^{\circ}$  C. The result of the experiments is much affected by the sensibility of the skin, being much more marked when the skin is sensitive, as it is in light-coloured or white female rabbits.

T. L. B.

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**New Method of Demonstrating and Measuring the Action of Pepsin.** By A. GRUENHAGEN (Pflüger's Archiv., v, 203).

IN order to make the action of pepsin visible to a large class, the author recommends that a piece of thoroughly moist blood-fibrin be placed in 0.2 per cent. hydrochloric acid, till it swells up to a stiff jelly, and then laid on a funnel either with or without a filter. After the superfluous acid has drained off, a few drops of the digestive fluid, such as glycerin extract of pepsin are to be added to the jelly with a pipette. In about two minutes the fibrin becomes liquefied by conversion into peptone, and begins to drop from the funnel. The rapidity with which the drops fall indicates the intensity of the digestive action. To show the comparative digestive powers of concentrated and dilute solutions of pepsin, equal quantities of the fibrin-jelly are to be laid on funnels of equal size, and equal quantities of the different digestive fluids added to each. The more dilute the solutions, the more slowly do the drops fall. To show the influence of temperature on digestion, pieces of fibrin are to be laid in funnels in the same way, one being kept at the temperature of the room, and the others warmed to the desired degree by a sand or water-bath, with a perforated bottom, and then the digestive fluid added. The rapidity with which the drops fall increases with the temperature up to a certain maximum, above which it sinks rapidly, and cannot be brought up to its former rate by rapid cooling.

T. L. B.

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**Physiological Action of Beef-tea and Potash Salts.** By GUSTAV BUNGE (*Pflüger's Archiv*, iv., 235—282).

THE author's experiments lead him to conclude that the common opinion that beef-tea and extract of meat are as valuable articles of diet as tea, coffee, or alcohol, is totally unfounded; that the refreshment they give is only due to their warmth and pleasant taste; and that their chief value consists in their enabling a person to take with appetite a larger amount of dry or tasteless food than he could otherwise do. The statements of Liebig that the addition of meat-extract to vegetable food increases its nutritive value, and that the extractive matters of meat, especially creatine and creatinine, are the materials for muscular work, have been disproved by Voit and Meissner; and the idea that beef-tea and meat-extract are beneficial on account of the salts they contain, is an unlikely one, as these salts are already present in excess in ordinary food. It has been said, however, that they do good by acting as stimulants, like coffee, tea, and alcohol; and this seemed to be confirmed by the experiments of Kemmerich. He found that small doses of meat extract quickened the pulse; but large ones produced paralysis of the heart, and death. This action on the circulation he attributed to the potash-salts contained in the extract, as the ash alone produced the same effects as the quantity of extract from which it had been obtained.

As Traube, Guttman, and Podkopaew found that potash-salts rendered the pulse slower, but never quicker, and as Kemmerich's experiments on man gave an indefinite result, and the only animals he used were rabbits, Bunge investigated anew, in Professor Schmiedeberg's laboratory, the action of meat-extract and of potash-salts on man, dogs, cats, and rabbits. On taking himself, or introducing into the stomach of a dog, a quantity of meat-extract mixed with flour, and containing 5 to 6 grams of potash-salts (a quantity sufficient to kill two rabbits), he found that no effect whatever was produced on the pulse or on the temperature. Large doses of meat-extract first quickened the pulse and then paralysed the heart. The quickening does not seem to be due to the potash-salts, but to the introduction of fluid, and the consequent distension of the stomach: for the author found that muzzling the animal, introducing a tube into the œsophagus, and distending the stomach with water, alike quickened the pulse. When a solution of salt or sugar was used instead of water, the quickening lasted longer, because the fluid was more slowly absorbed, and the distension less quickly removed. Extract of meat, deprived of five-sixths of its potash-salts by means of tartaric acid, caused death, not like the potash-salts by paralysing the heart, but probably by desiccating the tissues. Sodium phosphate has a similar action. This is diminished by injecting water subcutaneously, after the sodium phosphate has been introduced into the stomach.

Potash salts injected subcutaneously into rabbits quicken the pulse by causing pain; but they do not alter either the number or force of the heart-beats in dogs or cats, either when given subcutaneously or by the mouth, or by injection into the blood, except when given in fatal doses, and then they lessen the beats both in number and force. They have little action on the temperature or blood-pressure.

The poisonous action of potash-salts has been much exaggerated. When injected almost directly into the heart through the jugular, a very small dose will cause death (0.1 gram in a dog weighing 5300 grams) by cardiac paralysis; but very large doses are required when administered subcutaneously, or by the mouth. Bunge reckons the amount of potash-salts taken daily in potatoes by many Irish labourers at 100 grams. It is probably impossible to produce cardiac paralysis in man by potash-salts introduced into the stomach, as the large quantity necessary would be ejected by vomiting.

T. L. B.

### Composition of Urine. (Pharm. J. Trans. [3] ii, 705.)

In a paper recently published, Wanklyn gives the result of some interesting experiments he has made on the chemical examination of urine. Pointing out the fact that determinations of the specific gravity of urine are frequently faulty through inattention to the temperature, and that a slight difference in specific gravity corresponds to a great alteration in solid contents, he recommends that they should be replaced or supplemented by the determination of the solids left on evaporation, and the ash left on incineration. He also recommends operating on small quantities, and states that although the urine varies, the proportion between the organic matter and the mineral matter in healthy urine is remarkably constant. Thus, in five cases where 100 cubic centimeters of urine of healthy persons were examined, he found:—

Mineral matter.	Organic matter.	Ratio.
I.—1.50 grams.	2.53 grams.	1 : 1.69
II.—1.40     "	2.34     "	1 : 1.67
III.—1.48     "	2.38     "	1 : 1.61
IV.—0.60     "	0.80     "	1 : 1.33
V.—2.00     "	2.40     "	1 : 1.20

In these specimens the proportion of organic matter to ash never exceeded 1.7. But in some urine from a patient suffering from a disease of the kidneys, the quantities of mineral and organic matters in 100 cubic centimeters were—mineral matter, 0.63 grams; organic matter, 2.03 grams: ratio, 1.00 to 3.22.

## Chemistry of Vegetable Physiology and Agriculture.

**Further occurrence of Inosite in the Vegetable Kingdom, and its Convertibility into Paralactic Acid.** By Dr. HILGER (Ann. Chem. Pharm., clx, 333—338).

VOHL was the first to discover inosite in plants, and it has since been found in numerous members of the vegetable kingdom.

Hilger, in his investigations on wine and grape-juice, has found inosite largely in the grape. It was obtained in watery solution after separa-



tion of the other constituents of grape-juice by baryta and lead acetate (for details see original paper).

The watery solution after concentration was decomposed by a mixture of ten parts alcohol and one of ether. At the end of five or six days at a low temperature, the solution deposited crystals having the characters of inosite, and giving the inosite reaction with nitric acid and calcium chloride. With a view to throw light on the possible source of paralactic acid in muscle, fermentation was induced by means of putrid cheese, and the products were tested for lactic acid. The zinc and calcium lactates obtained, showed, by their solubility and amount of water of crystallisation, that the acid was paralactic acid. So also with the copper salt. In addition, Hilger has obtained malonic acid from this by oxidation, a proof that the acid is paralactic and not ordinary lactic acid, which yields only formic and acetic acids when treated in the same way.

D. F.

### Saccharine Matter found on the Leaves of a Lime Tree.

By M. BOUSSINGAULT (Compt. rend., lxxiv, 87—90).

IN July, 1869, at Liebfrauenberg, the leaves of a lime tree were found coated on their upper surface with a viscous matter, extremely sweet, and abundant enough to fall, when exposed to the sun, in drops on the soil; in the shade, however, soon resumed its viscous state.

This sweet matter, after the removal of its albumin, mucilage, &c., by lead acetate, was found to have a composition similar to that of manna from Mount Sinai, analysed by Berthelot—

	From Lime tree.		Manna from Sinai.
	July 22.	Aug. 1.	
Cane sugar.....	48·86	55·44	55
Inverted sugar ....	28·59	24·75	25
Dextrin .....	22·55	19·81	20
	100·00	100·00	100

The diseased leaves were coated with a much larger quantity of the sweet matter than the healthy ones, and that exuded by the latter was free from dextrin.

J. B.

### Alcoholic Fermentation of Milk-Sugar. By M. BLONDLOT (Compt. rend., lxxiv, 534—536).

MILK, under favourable circumstances, produces a special alcoholic ferment which differs from ordinary yeast in requiring agitation to enable it to become active, in operating in an intermittent manner, requiring rest and agitation alternately, and in not manifesting any action below 20°. A temperature of 30° to 35° is the best for the purpose. No carbonic acid gas is evolved until the milk is shaken, and

the quantity diminishes gradually as the fermentation approaches completion. When the fermentation has ceased, an addition of milk-sugar or of ordinary glucose, causes it again to become active. The alcohol produced has an agreeable taste, but is apparently contaminated with a little butylic alcohol.

J. B.

**On the Ferment which effects the Conversion of Cane-sugar into Grape- and Fruit-sugar.** By F. HOPPE-SEYLER (N. Repert. Pharm., xx, 764).

THIS ferment, separated from beer-yeast, forms a white powder, which is soluble in water, and may be preserved unaltered in the dry state under alcohol. Living beer-yeast does not give it up to water, but if the yeast be killed by addition of a little ether, the ferment may easily be extracted by water and separated from the solution. The aqueous solution quickly effects the transformation of the sugar.

**Influence of Germination on the Amount of Fat in Seeds.**

By A. VOGEL (Ber. d. K. bayer. Akademie d. Wiss. 1871. Heft II. —N. Repert. Pharm. xx, 693—696).

THE author finds that the loss of fat during germination is very small. He took equal weights of whole seeds. One part was exhausted with ether, and the fat determined the other part fully germinated, and then treated with ether: the percentages of fat found were as follows:—

	Wheat.	Rye.	Barley.	Cress.	Oats.
Original seed .....	2·094	2·234	2·310	3·980	4·250
Germinated seed .....	2·000	2·120	2·200	3·660	4·086

Cress seed, when completely exhausted by ether, is still capable of germinating in a perfectly normal manner. Of the cereals, barley is most affected by the removal of the fat; germination is in this case slower, and not so perfect, as in the fresh seed.

R. W.

**Analyses of Food-stuffs.** By J. MOSER (Versuchs-Stationen Organ, xiv, 147—148).

THE food-stuffs analysed were principally average samples of the hay and oats used in eight first-class studs in Austrian Hungary; of these samples the mean composition is given below, also the highest and lowest percentages found. The forest-hay is obtained from the Alpine regions; it is rich in aromatic herbs, and is highly valued.

Food stuff.	Water.	Protein.	Crude fat.	Crude fibre.	Non-nitrogenous extractive matter.	Ash (minus C, CO <sub>2</sub> and sand).	Potash.	Phosphoric acid.
Hay, highest percentages .....	14.45	14.43	6.69	33.33	40.12	7.86	2.51	.61
Hay, lowest percentages .....	11.30	10.48	3.74	21.18	29.99	5.38	1.55	.35
Hay, mean of eight samples .....	13.13	12.57	4.86	28.59	34.36	6.48	1.98	.43
Forest hay .....	14.56	14.34	6.92	29.23	30.70	6.48	—	—
Oats, highest percentages .....	14.42	18.51	7.11	13.39	56.24	1.84	.70	.91
Oats, lowest percentages .....	11.27	10.10	5.72	9.81	47.90	3.08	.38	.68
Oats, mean of ten samples .....	12.76	14.08	6.45	11.24	51.84	3.62	.55	.78
Potato refuse (spirit factory) ....	96.05	.79	.23	1.40	1.12	.41	—	—
Iceland moss .....	15.04	4.47	5.79	1.49	72.03	1.19	—	—

R. W.

**Soil Statics and Soil Analyses.** By HERMANN V. LIEBIG  
(Zeitschr. d. landw. Vereines, February, 1872).

THE science of the chemical statics of soil depends essentially on accurate soil analyses. Analysis must point out which of the plant-foods are deficient, and thus suggest the manure which shall bring about a proper relation between the nutritive matters of the soil. When this has been done, maximum crops will be obtained with minimum applications of manure, and the farmer will be able to ascertain by simple calculations how to maintain the soil in this favourable condition. To be able to interpret soil analyses, it is necessary to ascertain by experiment what amount of each plant-food a soil must contain in order to produce full crops; these preliminary inquiries have never been made, from a belief that analysis was not a sufficiently accurate means of investigation. Discrepancies in soil analysis depend very much on the manner in which the soil is exhausted by acid; the author believes treatment with dilute acetic acid, and with dilute nitric acid for determination of phosphoric acid, give the best indication of the *available* plant-food present. He gives analyses, made by his method, of five soils from Mr. Lawes' experimental wheat field, which had, at the date of sampling, received known quantities of manure for 22 years, and from which the crops removed were also known; the samples represented the first 9 inches of the surface soil.



100 parts of soil contain :—	Soluble in dilute hydrochloric acid.	Soluble in dilute acetic acid.				
	No. 3. Unmanured.	No. 3. Unmanured.	No. 10a. Ammonia salts.	No. 5a. Cinereal manure.	No. 7a. Cinereals and Ammonia.	No. 2. Farm-yard manure.
Hygroscopic water ..	1·825	1·825	2·561	1·949	2·072	1·810
Organic matter.....	5·362	5·363	4·272	4·470	5·380	6·212
Silicic acid .....	·434	·065	·064	·067	·066	·084
Ferric oxide and alumina..... }	4·463	·100	·139	·182	·100	·116
Lime .....	2·298	2·065	2·227	2·410	2·232	1·785
Magnesia .....	·092	·028	·028	·026	·031	·025
Potash .....	·085	·015	·013	·038	·039	·041
Soda .....	·066	·012	·013	·009	·011	·019
Sulphuric acid .....	·015	traces	·002	·006	·011	·008
Phosphoric acid in nitric acid extract .....	·075	·075	·076	·108	·126	·093

The lime in these soils is principally the residue of long previous dressings of chalk: the amount is therefore irregularly distributed. If all the phosphoric acid removed in the crops has come from the surface soil, the unmanured plot must have originally contained ·084 per cent.; a good wheat soil should contain, as a minimum, ·1 per cent. Calculating from the above analyses, it appears that most of the unused phosphoric acid applied to 7a and 5a, remains in the surface soil, but that more than half of the potash has passed below the first 9 inches; the loss of sulphuric acid by drainage is very much greater. For want of knowledge of the composition of a soil, superphosphate is perhaps often employed for fodder crops when sulphates alone are needed. The above results prove that analysis will plainly indicate alterations in the food-constituents of soils. This mode of investigation should be extensively employed.

R. W.

### Transformation of Nitrous Acid in Soil. By CHABRIER (Compt. rend., lxxiii, 1480—1483).

WHEN soil, freed by washing from nitrates and nitrites, is watered with a very dilute solution of ammonium nitrite, and allowed to dry after each watering, it is found to contain large quantities of nitric acid; moreover the total quantity of nitrous and nitric acids found in the soil greatly exceeds the amount applied as nitrous acid, showing that ammonia, or some other form of nitrogen, has been oxidised.

When a very dilute solution of an alkaline nitrite is allowed to filter slowly and continuously through soil (the experiment described lasted 101 days), the drainage-water at first contains both nitrous and nitric acids. The nitrous acid soon ceases to appear, and the nitric acid gradually diminishes, till at last neither nitrous nor nitric acid is found

in the drainage-water. On comparing the amount of nitrite applied, with the quantity recovered as nitrous or nitric acid in the drainage-water, and in the soil itself after the experiment, it becomes evident that a large proportion of the nitrite has disappeared, and remains unaccounted for.

Further researches are promised.

R. W.

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**Chemical Studies upon the Moors (Landes) of Brittany.**

By A. BOBIERRE (Compt. rend., lxxiv, 375).

THE soil in question is chiefly composed of silica and organic matter. Plants growing on the uncultivated land yield ashes remarkably poor in alkaline salts. The ash of heather contains but 3.8 per cent., and the ash of gorse 7.25 per cent.; while gorse grown on similar land treated with lime and farmyard manure yielded an ash containing 13.5 per cent. The ash of a young pine growing on the moor land gave 23.5 per cent. of alkaline salts.

R. W.

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**Preservation of Grain in a Vacuum.** By LOUVEL (Compt. rend., lxxiv, 421—426).

THE storing of grain, biscuit, or flour, is attended with considerable loss, chiefly from the attacks of weevils. The author proposes to store grain, &c., in large, upright, iron cylinders, having openings at top and bottom for the entrance and exit of material. When these are filled, a vacuum of about 10 cm. is produced in the cylinders by means of an air pump; this effectually destroys insect life, and also dries grain which might have been stored in a damp state. The result is a perfect preservation of the material.

R. W.

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**Examination of Rye Flour for Foreign Admixtures.** By C. SOMMER (Arch. Pharm. [2], xlix, 1—6.)

THE only point of special interest in this paper is the discrimination of barley-starch from rye, or wheat-starch. The flour is placed on a glass slide, and moistened with water; a covering glass is laid upon it; and a single drop of oil of vitriol added. If now viewed with a magnifying power of 200, the starch-grains of wheat and rye are seen to dissolve in a uniform manner; but the grains of barley starch, after losing their external coat, break up into a number of polyhedrons before their solution is completed.

R. W.

## Analytical Chemistry.

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**Litmus Paper as a Reagent.** By CHARLES BULLOCK (Pharm. J. Trans. [3], ii, 704).

IN using litmus paper as a reagent to detect the presence of acids and alkalis, the question sometimes occurs, "what amount of acids or alkalis is necessary to give a distinct change of colour to the test paper?"

The following are the results of a few experiments made with the view of answering the question, at least approximately:—

*Blue litmus paper* should be distinctly blue, but not of a deep shade. The directions given by Fresenius in his "Qualitative Analysis," will afford a sensitive paper; when carefully made it, affords the reactions with one drop of acetic acid No. 8 (30 per cent. acid) in the following amounts of water:—In 4 ounces of water it turns red immediately; in 6 ounces, completely red in one-half minute; in 10 ounces, changes on the edges in a quarter of a minute, and is completely reddened in one minute; in 13 ounces it is completely red in a minute and a half, and remains red when dry. In 16 ounces of water the limit of distinct reaction is found. *Reddened litmus paper.*—Reddened litmus solution should have a purple red colour, and the paper, when dry, a distinct red colour free from blue. With one grain of anhydrous carbonate of soda in 32 ounces of water, the paper turns blue in one minute; in 56 ounces of water, in three minutes; in 64 ounces of water, in four minutes; in 80 ounces of water, in seven minutes. The limit of distinct reaction is attained with 1 grain of sodium carbonate in 160 ounces of water.

In making the above experiments the paper was submerged in the liquid.

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**Application of the Sprengel Mercurial Pump to the Analysis of Coke.** By JOHN PARRY (Chem. News, xxv, 98—100).

DR. PERCY and others have already called attention to the fact that the elementary analysis of the best burned coke invariably shows a loss of carbon, the loss being so constant that it is generally assumed to be due to the presence of gaseous matter; by inference oxygen and nitrogen. The author finds that coke also persistently retains hydrogen; that different varieties of coal require different degrees of heat to expel their volatile constituents, and that even at a white heat, it is often impossible to free coke entirely from gaseous matter.

20 grams of gas coke, which had not been specially heated to a very high temperature, were placed in a combustion tube, and heated in the vacuum of the Sprengel pump for several hours, the gases being collected and tested from time to time.



At the expiration of  $2\frac{1}{2}$  hours, 301.5 c.c. of gas were obtained, containing—

CO <sub>2</sub> .	O.	CO.	H.	CH <sub>4</sub> .	N.
22.80	0.00	13.49	50.00	13.80	0.00

After seven hours' heating, 586 c.c. more gas were collected. The marsh-gas had now entirely disappeared, while the ratio of hydrogen to carbonic anhydride had greatly increased, 93.45 per cent. of the total gas being hydrogen. The heating was continued for several hours longer, during which time the percentage of hydrogen slightly decreased, with a corresponding increase of carbonic oxide and carbonic anhydride. Towards the termination of the operation, a small quantity of nitrogen was liberated. The total gas obtained from 20 grams of coke, after  $14\frac{1}{2}$  hours' heating, was 1117.2 c.c.

A sample of coke, prepared from a different vein of coal was next examined. 20 grams were taken as before :—

		Gas.	CO <sub>2</sub> .	O.	CO.	H.	N.
Heated 2 hours ..	28 c.c.	77.12	—	4.153	0.00	17.78	
Again 2½ „ ..	32 „	33.22	—	0.00	34.56	31.00	
	—	—	—	—	—	—	
4½ „	60 „						

The coke from this specimen of coal differs from the previous sample, not only in containing nitrogen, but also in the ratio of hydrogen to carbonic anhydride, the latter gas greatly predominating. This coke is in good repute for iron-smelting, while sample No. 1 is never used, having been found unfit for use in the blast furnace.

A number of similar experiments were performed with samples of coke derived from various sources ; the results of all so far agree that carbonic oxide, carbonic anhydride, hydrogen, and nitrogen were the only gases found, oxygen and cyanogen being invariably absent ; however, no two samples of coke evolve exactly the same volume of gas, or gas of the same composition.

The author thinks it premature to hazard any suggestion as to the effect of the gases shown to be contained in coke, when used in the blast furnace. It is, however, probable that they are only eliminated at a very high temperature, the carbonic anhydride possibly being retained up to the fusing point of cast-iron. He has, however, invariably found that what is termed weak coke, *i.e.*, a coke of which a greater quantity than usual is required to smelt a given quantity of ore, always contains the largest proportion of hydrogen, and that nitrogen is absent, or present only in very small quantity.

J. W.

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**An Azotimeter.** By A. HOUZEAU (Ann. Chim. Phys. [4], xxiii, 469—475).

THIS is a portable apparatus for performing the ordinary soda-lime process. The open end of the combustion tube is connected by caoutchouc with a delivery tube having a fine point; this tube is bent at

right angles, and passes to the bottom of an upright vessel containing 100 c.c. of water coloured by litmus. The amount of ammonia evolved is determined from the quantity of standard acid required to neutralise the water. The neutralisation by acid is carried on during the progress of the combustion. The author recommends this method for the analysis of manures, and describes it as more speedy than that usually employed, and quite as accurate.

R. W.

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**Estimation of Nitric Acid.** By A. WAGNER (Dingl. Polyt. J., cci, 423—426).

INSTEAD of determining (*Chem. Soc. Journal*, 1871, p. 753) the chromic acid formed by the fusion of nitre with chromic oxide and sodium carbonate in an atmosphere of carbonic anhydride, Wagner now proposes to collect the nitric oxide evolved over mercury by charging the gas-tube with a standard solution of sodic hydrate and oxygen gas. The combustion is effected in a manner analogous to an ordinary nitrogen determination by Dumas' method. When no more oxygen is absorbed on agitation of the liquid, an aliquot part of the soda-solution is titrated back with normal sulphuric acid.

In order to determine nitric acid in potable waters, the author evaporates with sodic carbonate and pure potassic permanganate; the latter partly destroys the organic matter, partly converts it into oxalic acid, which is not further acted upon in alkaline solution, but is readily oxidized in an acid solution. It is recommended to have always sufficient permanganate present to produce a deep rose-coloured solution. The concentrated saline residue is then filtered, and, when cold, rendered just acid with dilute sulphuric acid, whereby the oxalic acid is destroyed. Slight excess of permanganate solution should be added before rendering the solution again alkaline by means of baryta-water. A few drops of sodic carbonate are added to the solution, filtered, evaporated to complete dryness, and the saline residue mixed with excess of chromic oxide, and heated as described.\*

W. V.

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**Determination of the Temporary Hardness of Waters.**

By A. WAGNER (Dingl. Polyt. J., cci, 426—427).

To avoid the errors arising from determining the temporary hardness in waters rich in magnesia salts, by Clarke's soap-solution, the author proposes to add oxalic acid to the water (250 c.c.), heated to boiling till the whole of the carbonic acid in the calcic and magnesian carbonates has been displaced, the excess of oxalic acid showing an acid reaction with litmus-paper. He employs a standard solution containing 2.250 grms. of pure crystallised oxalic acid per litre, 1 c.c. of which corresponds to .001 grm. of  $\text{CaO}$ , or .001786 grm. of  $\text{CO}_3\text{Ca}$ ; the magnesia

\* The difficulty of absorbing the large quantities of carbonic anhydride required to displace, first the air, and subsequently the nitric oxide formed, by a dilute standard solution of soda, militates against this method.—W. V.

being, as in Clarke's soap-test method, expressed in lime-units. The litmus-paper should be prepared by means of white note-paper, and not from filter-paper, and its delicacy should be determined by adding to 250 c.c. of distilled water, gradually, oxalic acid solution, till a drop of the water just reddens the litmus-paper. The quantity of acid so employed is deducted from the oxalic acid used to decompose the earthy carbonates. The author mentions incidentally, that a drop of carbolic acid water added to litmus-solution, most effectually prevents its decomposition, even in close vessels.

The results obtained, and checked by gravimetric methods, are very satisfactory.

W. V.

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**A Delicate Test for Nitric Acid in Water.** By EDWARD NICHOLSON (Chem. News, xxv, 89).

THE ferrous sulphate test being uncertain for quantities less than 1 in 100,000, a modification of Kersting's brucine test has been tried instead. 1 c.c. of the water is evaporated to dryness, the residue moistened with a drop of pure sulphuric acid, and a fragment of brucine moved about in the liquid; .0001 gram of nitric acid per litre was thus readily detected by a rose coloration.

C. G. S.

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**On the Normal Constituents of Rain-water and Snow, and the Estimation of the Nitric Acid.** By FR. GOPPELSROEDER (J. pr. Chem. [2], iv, 139—154).

IN a lengthy and verbose memoir, the author passes in review the different reagents for recognizing in rain-water or snow the hitherto discovered normal constituents, namely, hydrogen dioxide, nitrous and nitric acids, and ammonia. Passing over his theories about *minus* and *plus* ozone, or ozone and antozone, we merely note that he advocates Marx's improved method for determining small quantities of ammonium nitrate in rain-water and snow in the presence of hydrogen dioxide, by means of sulphindigotic acid.

His experiments\*—98 in number—extend over a period of nine months,—from October, 1870, to June, 1871, and are summed up in the following table, containing the maximum and minimum amounts of nitric acid—present as ammonium nitrate—in 1,000,000 parts of rain or snow-water :—

\* It is to be regretted that none of these experiments were checked by the author by any of the more accurate, although more tedious, methods known for the estimation of nitric acid.—W. V.



Months 1870-71.	Total amount of rain and snow-water.	Minimum		Maximum	
		Amount contained in 1,000,000 parts of the collected rain or snow-water.			
		Nitric acid.	Ammonium nitrate.	Nitric acid.	Ammonium nitrate.
October, 1870.....	101·2 mm.	trace	trace	13·6	20·1
November „ .....	123·9 „	·5	·7	1·2	1·8
December „ .....	91·2 „	·4	·6	5·3	7·8
January, 1871 ....	37·4 „	3·1	4·6	5·3	7·8
February „ .....	38·5 „	2·2	3·2	4·4	6·5
March „ .....	27·5 „	2·6	3·8	12·3	18·2
April „ .....	107·4 „	2·2	3·2	4·6	6·8
May „ .....	41·3 „	2·2	3·2	10·	14·8
June „ .....	114·5 „	2·3	3·2	6·2	9·1

Former observers, among whom Barral, Bobierre, Boussingault, Bineau, and Knop, found from 0·1 to 16 parts of nitric acid.

The author recommends the four following tests for ascertaining the sanitary condition of atmospheric waters:—

1. Examining quantitatively for hydrogen dioxide by means of tincture of guaiacum and green vitriol.
2. Schoenbein's test for nitrous acid by means of potassic iodide and starch in an acidulated solution.
3. A quantitative test for ammonia and ammonium salts respectively, by means of a solution of corrosive sublimate, and a solution of potassic hydrate or carbonate.
4. A quantitative estimation of the nitric acid by means of a standard solution of sulphindigotic acid.

When more than mere traces of nitrites are present in the waters, they should be determined by means of a solution of permanganate in presence of free acid ( $\text{SO}_4\text{H}_2$ ).

The author records also an extensive series of nitric acid estimations by the above method, in pump and spring waters of the town of Basel; the amounts ranging from ·001 to ·4004 grm. per litre.

Referring to an obvious objection raised by Scheurer Kestner (*Bulletin de la Société industrielle de Mulhouse*, June, 1870, page 324), that nitrites act upon indigo-solutions simultaneously with and in like manner to nitrates, the author promises further experiments. Although he points out the rarity of the occurrence of the nitrites in good spring waters, and the changeable and transient nature of nitrous acid—a mere intermediate product of oxidation, between the nitrogen of the ammonia on the one hand, and that of the nitric acid on the other,—he nevertheless admits that a water containing more than mere traces of nitrites is unfit for drinking purposes.

**Analysis of Phosphatic Manures.** By R. FRESSENIUS, C. NEUBAUER, and E. LUCK (*Zeitschr. f. Anal. Chem.*, x, 133—158).

OF the methods of analysis in common use, the molybdenum method is the most accurate, and the only one perfectly satisfactory under all circumstances; it should be performed as previously directed (*Zeitschr.* vi, 403), omitting, however, the correction for the solubility of ammonio-magnesium phosphate. The ammonia solution of the molybdenum precipitate should be nearly neutralised with hydrochloric acid before adding the magnesia-mixture, a little dilute ammonia being afterwards added. The bismuth, uranium, lead, mercury, and tin methods, are admissible only when iron and aluminium are absent; in the presence of either of these bodies, the methods in question can only be used with serious modifications, which rob them of all their special advantages. The use of tartaric or citric acid, to keep iron and aluminium in solution during the precipitation of phosphoric acid by magnesia, does not yield very satisfactory results, since basic magnesium tartrate or citrate is often precipitated with the phosphate,\* and because the solubility of the ammonio-magnesium phosphate is increased by the presence of ammonium tartrate or citrate.

The volumetric uranium method, as ordinarily used, is trustworthy only when alkalis and magnesia are the only bases present. If citric acid is used to keep iron and aluminium in solution during the titration, some uncertainty is introduced, as free citric acid increases the solubility of uranium phosphate, and thus tends to give low results, while ammonium citrate, by diminishing the delicacy of the ferrocyanide-test, tends to give high results. If lime be present the results are apt to be low, since calcium phosphate partially separates from an acetic acid solution on heating, and thus a portion escapes the action of the uranium. The authors get rid of this error by reversing the process, and add a cold acetic solution of the phosphate to a hot solution of uranium, till the ferrocyanide-test just ceases to act.

When nitric acid acts on a phosphorite, the greater part of the iron remains undissolved, and with it a small portion of the phosphoric acid. Cold 5 per cent. sulphuric acid (Graham's method) dissolves very little iron, and all but .1 per cent. of the phosphoric acid. Hydrochloric acid takes up the whole of the phosphoric acid and iron. The authors recommend solution in hydrochloric acid, followed by the molybdenum method, in all cases where scientific accuracy is desired; but for ordinary use the following method is recommended as very exact, and occupying far less time.

110 cc. of 5 per cent. sulphuric acid are taken: 5 grams of the very finely-ground phosphorite are placed in a mortar, rubbed slowly with some of the acid till brought to a soft paste, then diluted with water, and the suspended matter is decanted into a flask graduated for 253 c.c., the residue being treated as before. When both phosphorite and acid have been thus brought into the flask, the whole is agitated from time to time during four hours. The flask is next filled to the mark: it

\* I have never obtained any precipitate by treating magnesia-mixture with citric acid, though varied conditions have been tried; with tartaric acid, on the contrary, it is easy to obtain a precipitate.—R. W.

then contains 250 c.c. of *fluid*; and the solution is filtered. 100 c.c. of the filtrate are placed in a flask graduated for 200 c.c., treated with excess of caustic soda, and then with acetic acid, till it ceases to diminish the precipitate; the flask is then filled to the mark, and after standing in the cold the solution is filtered; the precipitate is weighed, and reckoned as ferric phosphate. The phosphoric acid in the solution is determined by the improved volumetric uranium method already mentioned. The known quantity of uranium acetate employed is mixed with sodium acetate and acetic acid, and kept at a temperature of  $30^{\circ}$ – $40^{\circ}$  during the titration.

In the analysis of superphosphate the soluble phosphate is best separated according to the directions given in *Zeitschr.*, vii, 304; its quantity should be determined by the molybdenum method, or by that above described.

Superphosphates also contain "reduced phosphates," resulting, according to some, from the action of monocalcic phosphate on oxide of iron or alumina; according to others, from the action of the same body on undecomposed tricalcic phosphate: for the estimation of these reduced phosphates, sodium bicarbonate, and ammonium oxalate, have been confidently recommended. The authors took the precipitate obtained by adding excess of ordinary sodium phosphate to calcium chloride (chiefly dicalcic phosphate) as a type of reduced phosphate. Prolonged boiling with sodium bicarbonate only removed about half the phosphoric acid present in this substance; half an hour's boiling with ammonium oxalate removed more than  $\frac{9}{10}$ ths of the phosphoric acid; but, unfortunately, ammonium oxalate also acted energetically upon natural phosphorite. A solution of neutral ammonium citrate, sp. gr. 1.09, was found to answer the purpose required; it had practically no action on natural phosphorite, and decomposed the precipitated phosphate almost completely. The authors propose to estimate reduced phosphates by exhausting 2 grams of superphosphate with cold water, bringing the residue to fine powder, and digesting it for half an hour with 100 c.c. of ammonium citrate at a temperature of  $30^{\circ}$ – $40^{\circ}$ . Instead of determining phosphoric acid in the solution thus obtained, which would involve previous destruction of the citric acid, it is better to determine phosphoric acid in the unacted-on residue; this, in conjunction with a determination of soluble phosphate, and of total phosphoric acid, will give the reduced phosphates by difference.

Test experiments are given throughout the paper.

R. W.

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### New Method of Detecting Arsenic for Pharmaceutical Purposes. (*Dingl. Polyt. J.*, ccli, 385.)

A LITTLE stannous chloride and 4 to 6 c.c. of pure hydrochloric acid of sp. gr. 1.12, are shaken together in a test-glass, till the salt is dissolved, and to the solution in the glass is cautiously added, drop by drop, 2 to 3 c.c. of a sample of concentrated sulphuric acid, which is to be tested for arsenic, the liquid being gently agitated after each addition. If no arsenic is present the solution remains colourless and clear, if it be present, a yellow coloration is produced, changing to brown, and



finally to dark greyish-brown. If a 500,000th part of arsenious acid be present, a faint yellow is the result, changing after half an hour to a brownish shade. This reaction is considered very little inferior in point of delicacy to that in the "Marsh-test."

W. S.

**The Assaying of Bismuth Ores, and Separation of Bismuth from other Metals.** By HUGO TAMM (Chem. News, xxv, 85—100).

THE subject is divided into two sections—1. The extracting or assaying of bismuth ores. 2. The refining of crude bismuth.

The reduction of an ore of bismuth, when free from admixture with other ores, is an exceedingly simple and well known metallurgical operation, but the direct separation of bismuth from ores containing a large proportion of copper is a problem which has always presented great difficulty, inasmuch as copper and bismuth behave in nearly every instance, in an identical manner with docimastic reagents. The author has, however, succeeded in devising a process which is capable of effecting readily and practically the separation of these two metals. He finds that, in presence of an alkaline flux, bismuth sulphide is instantly reduced by carbonaceous matter, whilst copper sulphide is unattacked. The application of this reaction is simple.

If the metals exist already in the state of sulphides, it is only necessary to fuse them with the ordinary reducing mixture, to which a little sulphur has been added, to prevent any desulphurisation of the copper by the alkali. The yield of bismuth will be found tolerably free from copper.

In the treatment of oxidated ores, the operation is conducted in a similar manner, but a larger amount of sulphur is required, since the whole of the metals have to be sulphurised. The following proportions are recommended for the flux:—Sodium carbonate, 5 pts. ; salt, 2 pts. ; sulphur, 2 pts. ; charcoal, 1 pt. Two or three parts of this flux are required for the reduction of three parts of ore.

In the extraction of bismuth by the sulphur-carbon process, there is a loss of about 8 per cent. of the bismuth contained in the ore. Although this loss is unavoidable, it is partly compensated by the elimination during the operation of a considerable quantity of arsenic, antimony, and lead, so that the crude metal obtained by this process is not so impure as the corresponding metal obtained by the direct reduction of the oxidated ore.

#### *Refining of Crude Bismuth.*

*Separation of Bismuth from Arsenic.*—The bismuth is melted at a bright red heat, under a cover of borax, and strips of iron are plunged into the molten metal. The arsenic rapidly combines with the iron, forming an arsenide, which rises to the surface of the metal. When the iron is no longer attacked, the whole is allowed to cool, and the bismuth while still fluid, decanted from the iron arsenide, which solidifies more rapidly.

*Separation of Bismuth from Antimony.*—The best way of separating

these two metals is by melting the alloy with a quantity of bismuth oxide, equal to three times the weight of antimony contained in the metal. The bismuth oxide is instantly reduced to the metallic state, while the antimony is converted into oxide. The latter, in combination with a little bismuth oxide, floats on the surface of the pure metal, whence it can be easily removed.

*Separation of Bismuth from Copper.*—The complete elimination of copper from bismuth is effected by treating the alloy at a low red heat, with potassium sulphocyanide. One part of a mixture of 8 pts. of potassium cyanide, and 3 parts of sulphur is thrown over 16 parts of the metal, melted at a low temperature. As soon as the reaction takes place, the crucible is covered, and when all deflagration has ceased, the metal is well stirred with a clay stirrer, the flux allowed to set, and the fluid metal poured out. The bismuth will be found perfectly free from copper.

The author has been unable to devise a process for the purification of bismuth from lead, which can be considered really satisfactory as a metallurgical operation.

J. W.

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**On the Methods of Sugar Estimation.** By W. PILLITZ  
(*Zeitschr. f. Anal. Chem.*, x, 456—463).

THE author has compared the methods of Fehling and Knapp. The latter method is based upon the reduction of mercury cyanide solution by grape-sugar, and not by cane-sugar, on boiling. As long as any cyanide is undecomposed, a drop of the solution placed on filtering paper, gives, if a drop of ammonium sulphide be held on a rod over it for a half minute, a brown spot.

These two methods the author has found to give very concordant results.

The method of estimating grape sugar by the amount of carbon dioxide given off whilst undergoing fermentation, has also been tested by the author, 100 parts sugar being supposed—as Pasteur says—to give off 46.7 parts  $\text{CO}_2$ . This method was found to give, for many reasons stated by the author, results much too low.

The polarisation method is regarded by the author as trustworthy, only when a solution of a sugar which turns the plane of polarisation in one direction is tested; if any substance influencing the direction of turning be present, besides the sugar, the results are not to be trusted.

The author also remarks that a sugar-solution exposed to the air, and tested at intervals, shows a less and less percentage amount of sugar.

M. M. P. M.

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**On the Solutions of the Compounds of Glycerin with Copper (or Bismuth) Oxide in Caustic Soda.** By JULIUS LÖWE  
(*Zeitschr. f. Anal. Chem.* x, 452—454).

THE author refers to a former communication regarding grape-sugar estimation by means of the compound of glycerin and copper oxide in

a caustic soda solution, and he now says that this solution, whether in the dark or in daylight, keeps unchanged.

To prepare the solution the author recommends that hydrated copper oxide, glycerin, and caustic soda-solution be warmed with a little water on the water-bath. He gives the following data:—

15.305 grm. hydrated copper oxide, 30 grm. glycerin, 80 c.c. soda-solution of sp. gr. 1.34, to be dissolved in 160 c.c. water, and the solution made up to 1155 c.c. Of such a solution 10 c.c. = .05 grm. dry grape-sugar.

Hydrated bismuth oxide may be substituted for copper oxide. 15 grm. basic bismuth nitrate and 30 grm. glycerin, gently heated on the water-bath with 60—70 c.c. soda solution of sp. gr. 1.34 and 130—160 c.c. water, form a clear solution which may be made up with water to 700—800 c.c. without precipitation.

From such a solution grape-sugar precipitates, on warming, grey, finely divided metallic bismuth. M. M. P. M.

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### Examination of Citric Acid for Crystals of Tartaric Acid. (Dingl. Polyt. J., ccii, 387).

HAGER has contrived the two following methods for this purpose. A solution of 4 grms. potassium hydrate in 60 c.c. water is mixed with 30 c.c. of 90 per cent. spirits of wine, and poured on one or two glass plates, so that the liquid stands not less than 6 mm. high. Small and large crystals of the citric acid to be tested are now placed in the solution, about 3 to 5 centimetres distant from one another. The plates are on no account to be disturbed. In two or three hours the citric acid crystals are nearly, if not quite dissolved, and in each of their places is left a small, delicate, white, powdery patch. The tartaric acid crystals, on the contrary, appear dissolved to a small extent only, whitish and opaque, and with either an enclosure of white acicular crystals, or surrounded by an aggregate of small crystalline groups, lying one upon another. The citric acid crystals, after several minutes under the action of the alkaline solution, appear clearer and more transparent, the tartaric acid crystals muddy and whitish. The second process consists in placing the crystals with the same precautions in a dilute, transparent solution of potassium permanganate, made strongly alkaline by addition of fused potassium hydrate. After one or two hours tartaric acid crystals, which as a rule are not quite dissolved, will be found to have left a yellow or colourless spot. Citric acid, on the contrary, gives a green colour, with a tinge of blue; the crystals are usually dissolved. The first plan is the best and safest; in either case the mode of procedure described must be strictly adhered to, or the results will be considerably modified. Perfectly pure citric acid gives no whitish spot, but the commercial acid never fails to do so.

W. S.

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### Detection of Piperine. By H. HAGER (Chem. Centr., 1872, p. 96).

AN alcoholic extract is treated with a drop of concentrated nitric acid, then warmed and cooled, and this treatment is repeated till the piperine



is obtained as dark-coloured drops floating in the liquid. This is cooled; a 10—15 per cent. solution of caustic potash is added; and the vapour given off on gentle boiling is passed into water, by which it is rapidly absorbed. The water smells strongly of ammonia and pepper, and gives the following reactions:—With potassium iodide a dark brown precipitate; with phosphomolybdic acid a light yellow precipitate soluble in excess of ammonia; with potassium-cadmium iodide a gelatinous; and with potassium-mercury iodide a white precipitate, easily soluble in dilute sulphuric acid. Mercuric chloride gives a white precipitate. With bromine water there is a cloudiness which passes away. With silver nitrate ensues a greyish brown precipitate, soluble in caustic ammonia, the solution, on boiling, giving reduced silver.

M. M. P. M.

**Use of Phenol for detecting Narceine and Curarine in Chemico-legal Investigations.** By F. SALOMON (*Zeitschr. f. Anal. Chem.*, x, 454—456).

*I. Narceine.*—After the usual treatment, the residue, which has been exhausted by alcohol, is taken up in water, and shaken with ether and amyl alcohol successively; or, if Dragendorff's method of testing for the two alkaloids be adopted, then the author recommends to treat first the acid, then the alkaline solution with petroleum ether, benzol, amyl alcohol, and chloroform.

The narceine is then partly dissolved in the amyl alcohol, where it is detected by evaporation, but chiefly in the alkaline watery solution. This is neutralised with dilute sulphuric acid, an equal volume of phenol is added, and the liquid shaken. The clear separated phenol solution is washed with a little water, and evaporated in a small basin; the residue is dissolved in water; the solution neutralised, and evaporated to dryness in the water-bath; the residue dissolved in absolute alcohol; and the solution is evaporated down. The narceine is thus obtained almost pure.

*II. Curarine.*—This alkaloid may be detected in a similar manner. After treatment with benzol, &c., the curarine remains entirely in the watery alkaline or acid solution; this is neutralised, treated with phenol, and evaporated; the residue is extracted with acidified water, neutralised, and evaporated; and this residue is dissolved in absolute alcohol, whereupon the alkaloid is obtained nearly pure.

M. M. P. M.

**New Process for the valuation of Aniline Colours.** By ARMAND MÜLLER (*Dingl. Polyt. J.*, ccii, 458—463).

TWO-TENTHS of a gram of the particular colour in a pure state is to be dissolved in 100 c.c. of collodion, and the solution poured over a clean glass plate laid at an angle of 60°. An equal weight of the material to be valued is to be dissolved in 50 c.c. of the same collodion and a drop or two poured on another glass plate at the same angle. If after drying the two films have an equal intensity of colour, the material obviously contains 50 per cent. of pure colouring matter; if, however, the second film be darker, the solution from which it proceeds is to be gradually let down by addition of measured quantities of the

collodion till it gives a film of the same depth of tint as the standard. The number of c.c. of collodion, employed in all, expresses the percentage of pure colouring matter.

C. H. G.

**Separation and Quantitative Determination of the different Cinchona Alkaloids.** By J. E. DE VRIJ (Pharm. J. Trans. [3], ii, 642—645).

THE process introduced by the author for the separation and quantitative determination of the cinchona alkaloids is based upon the following facts:—

1. The great solubility of quinine and amorphous alkaloid in ether, and the relative insolubility of quinidine, cinchonine, and cinchonidine in this liquid.

2. The great solubility of the iodosulphate of amorphous alkaloid in alcohol, and the very slight solubility of the iodosulphate of quinine (herapathite) in the same.

3. The difference of solubility in water between the tartrate of cinchonidine and the tartrates of cinchonine and quinidine.

4. The difference in solubility between the hydriodate of quinidine and the hydriodate of cinchonine in water and alcohol.

The application of these facts to the determination of the respective cinchona alkaloids is conducted in the following manner:—

5 grams at least of the pulverised mixed alkaloids are digested with 50 grams of ether, and filtered, whereby the alkaloids are separated into two groups.

*A. Part soluble in Ether.*—The ether is evaporated, the residue dissolved in 10 parts of proof spirit, acidulated with one-twentieth of sulphuric acid, and alcoholic iodine added until a precipitate is no longer formed. The quinine is thus precipitated as herapathite. One part of herapathite washed, and dried at 100°, represents 0·565 parts of pure quinine. The liquid separated from the herapathite is mixed with an alcoholic solution of sulphurous acid, then neutralised with caustic soda, heated on a water-bath to expel alcohol, and mixed with an excess of soda. The precipitate consists of amorphous alkaloid, with perhaps traces of quinidine and cinchonidine.

*B. Part insoluble in Ether.*—The insoluble alkaloids are dissolved in 40 parts of hot water with the aid of a little dilute sulphuric acid, the acid being so adjusted that the solution shall preserve a faint alkaline reaction. To this liquid, a solution of Rochelle salt is added, and the whole allowed to remain for twelve hours. The cinchonidine will be found separated as tartrate, which may be collected and dried at 100°. One part of this tartrate represents 0·804 parts of cinchonidine. The filtrate is mixed with a solution of potassium iodide, which precipitates the quinidine as a sandy crystalline powder, provided that the quinidine be not very small in quantity relatively to the cinchonine; otherwise the precipitate is often resinous. One part of the hydriodide dried at 100° represents 0·718 parts of anhydrous quinidine.

The liquid separated from the quinidine is precipitated by caustic soda, whereby the cinchonine is obtained; it is collected and dried as in the previous instances.

The author designates as “amorphous alkaloid” the dextrogyrate

substance soluble in ether. He thinks that it may possibly prove to be identical with Pasteur's quinicine.\*

J. W.

**Determination of Uric Acid.** By E. SALKOWSKI (Pflüger's Archiv., v, 210—222).

IN a former research Salkowski found that all the uric acid in urine was not precipitated by hydrochloric acid, but that a considerable additional quantity of acid could be afterwards obtained from the urine by precipitating the magnesia and lime with ammonia, then the uric acid with silver nitrate, and decomposing the latter precipitate with hydrogen sulphide. The silver precipitate obtained by this process was more stable when the uric acid was first precipitated in great part by hydrochloric acid than when the whole was thrown down as a silver compound. This he supposed to be due to the former precipitate being a combination of uric acid, magnesia, and silver, the magnesia in the urine not having been all precipitated by the ammonia, and the latter precipitate being a combination of uric acid and silver merely mixed with the double salt, the quantity in the urine being too small to form a double compound with the whole of the uric acid. The present research was undertaken with a view to discover what proportion of the uric acid was not thrown down by hydrochloric acid, so that an allowance could be made for it. Unluckily, however, it was found that the amount was not constant. In order to get all the uric acid thrown down as a double salt of magnesia and silver, the author precipitated the urine, partly freed from uric acid by hydrochloric acid, with ammonia and magnesia mixture instead of ammonia alone, filtered immediately, and then proceeded as before. By this change in the method of proceeding the silver precipitate is more stable, and it neither loses uric acid during washing nor does a reduction of the silver occur at the expense of the uric acid.

With a little practice the silver salt may be completely decomposed and any error from this source avoided. Any error from slight solubility of the precipitated uric acid in hydrochloric acid and in wash-water is very slight, and is counterbalanced by the colouring matter precipitated.

From a table of 28 experiments, the following are extracted :—

No. of experiment.	Urine in c.c.	Specific gravity.	Uric acid in 200 c.c.			Uric acid, absolute amount.
			By HCl.	By AgNO <sub>3</sub> .	Total.	
15....	1040	1·019	0·0275	0·031	0·0585	0·304
16....	880 not all	1·018	0·087	0·026	0·113	0·477
17....	1230	1·018	0·033	0·070 (!)	0·103	0·633
19....	1500	1·014	0 (!)	0·031	0·031	0·232
23....	—	1·018	0·037	0·044	0·081	—
26....	900 not all	1·017	0·0085(!)	0·059 (!)	0·0675	—

\* See page 106 of this volume.



The other experiments show that the uric acid not precipitated by hydrochloric acid, but precipitated by silver, is about 0.03. Higher amounts, however, occur, as in experiments 23, 26, and 17, in which the urine when tested only by hydrochloric acid seemed poor in uric acid, whereas it was really not so. In No. 23 only half the uric acid was precipitated by hydrochloric acid, and in 19 none at all.

Other experiments made by precipitating the urine with magnesia mixture, and then with silver nitrate, show that the numbers contained in the above table indicate the correct amount of uric acid, and that the error occasioned in the old method by its solubility is not compensated by the colouring matter thrown down with it.

The uric acid in urine cannot be estimated directly by estimating the silver in the silver precipitate, as this has not a constant composition.

T. L. B.

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### **Modification of Pettenkofer's Test for Bile Acids in Urine.**

By GUSTAV. STRASSBURG (Pflüger's Archiv., iv, 461—465).

ON testing icteric urine for bile acids by Hoppe-Seyler's methods, using Neumann's improved Pettenkofer's test, Strassburg was only able to get a yellow, but never a cherry or violet colour, which showed that the amount of bile acids present in the urine, even in cases of intense jaundice, is very small. He was able to detect them by a new and exceedingly delicate test, which has the further advantage of being easily applied by any physician at the patient's bedside. His process is:—Add to the urine a little cane sugar; dip a piece of filtering paper into the urine; allow it to dry; put a drop of pure sulphuric acid upon it, and allow the acid partially to run off. In a quarter of a minute a beautiful violet colour appears, which is best seen by transmitted light. By this means 0.00003 gram of glycocholic acid can be detected. The author attributes the great delicacy of the test to the circumstance that if water is absent, the charring which would otherwise occur and obscure the reaction, is prevented.

T. L. B.

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### **Determination of the Quality of Potable Waters.**

By G. BISCHOF (Zeitschr. f. Anal. Chem., x, 441—452).

CONTAINS descriptions and figures of the microscopic appearances presented by the evaporated residues of potable waters contaminated with various kinds of organic matter.

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*Instructions for the Examination of the Mineral Waters of Baden, undertaken at the instance of the Minister of the Interior of the Grand Duchy of Baden, under the direction of Prof. Bunsen (Zeitschr. f. Anal. Chem., x, 391—440).*

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## Technical Chemistry.

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**Notes on the Loss of Soda in Leblanc's Process.** By JAMES MACTEAR (Chem. News, xxv, 54).

### I. *Loss in the Sulphate Manufacture.*

1. As undecomposed salt. In well-conducted works this loss is never over  $2\frac{1}{2}$  per cent., and should not be under 2 per cent., as a loss of sulphuric acid would then ensue in furnacing.

2. As loss in the process. This loss may vary from 1 to 0.05 per cent.

### II. *Loss in Converting the Sulphate.*

1. As undecomposed sulphate; about 1.53 per cent. of the crude sulphate employed.

2. As sulphide, sulphite, hyposulphite, &c.; undetermined; can be prevented by taking due precautions.

3. Volatilised and lost mechanically; undetermined; can be prevented by taking due precautions.

4. Loss during lixiviation. Partly represented by insoluble and partly by soluble compounds left in the waste. The former sometimes attains 3 to 4 per cent. of the soda.

5. By secondary decomposition, as in the exposure of the ball soda to air and moisture, and the consequent formation of calcium sulphite, hyposulphite, and sulphate, which are converted into corresponding sodium salts, in the solution, also in the tanks, by the water being too hot, or the digestion too much prolonged, and the consequent formation of sodium sulphide. This constitutes the chief source of loss, amounting to 2.68 per cent. on the original soda.

6. By the presence of iron and the formation of the double sulphate of iron and sodium.

The average loss was found to be—

As neutral salts contained in the products .....	7.09
Total working loss .....	6.36

Loss in the process .... 13.45

W. S.

**Decomposition of Nitrous Sulphuric Acid by means of Glover's Towers.** By F. BODE (Dingl. Polyt. J., ccii, 448—453).

THE author considers that, when the material burnt in the ovens does not give rise to so much flue dust as to necessitate the use of a settling chamber, and so prevent the application of the heat of the ovens to the concentration of the acid produced, it is more economical to adopt Gerstenhofer's arrangement; and to decompose the acid from the Gay-Lussac's apparatus in the so-called "cascade."

C. H. G.

**The Industrial Out-turn of a Layer of Potassium Chloride at Kalutz in Galicia.** By A. JACOT (Dingl. Polyt., ccii, 477).

THE mine has been worked for many years for rock-salt, and about three years ago sylvine and kainite were discovered. The kainite gives by analysis  $\text{MgSO}_4$  30.04 per cent.,  $\text{KCl}$  29.46 per cent.,  $\text{NaCl}$  20.67 per cent., and  $\text{CaCl}_2$  1.27 per cent.

At present the yield of potassium chloride is over 81100 kilograms per day.

C. H. G.

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**Baryta Glasses.** By H. E. BEURATH (Dingl. Polyt. J., ccii, 422—433).

THE author having the opportunity, as director of some glass works near Dorpat, of making experiments on a working scale, has endeavoured to determine how far baryta can be advantageously used as a substitute for other "alkalis." Setting out with the admission that no glass which does not approach more nearly to the composition of  $\text{RO.3SiO}_2$  than to  $\text{RO.2SiO}_2$ , can be of practical value, on account of its easy decomposibility by water, &c., he has attempted to prepare glasses approaching the former composition, in which more or less of the "alkali" has been replaced by baryta. A glass containing silica 58.48, baryta 30.56, potash 10.96—melted well—blew easily—had a medium hardness, and considerable lustre. As compared with a similar lime-glass (*i.e.*, with an *equivalent* of lime in place of baryta), it was found to be of greater specific gravity and lustre, and more fusible; in resistance to chemical reagents it seemed to stand between lime and lead glass.

Attempts to increase the quantity of baryta in proportion to the other basic constituents, or to make the glasses more acid, resulted in obtaining masses which became devitrified on cooling. Although glasses containing no alkali can be prepared from silica, lime, and baryta, they are practically infusible if they contain more silica than corresponds to  $\text{RO.2SiO}_2$ , and these are so easily decomposed as to be worthless.

The author concludes that baryta can only be substituted for the lime, and not for the alkali of glass.

C. H. G.

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**Portland Cement.** By F. SCHOTT (Dingl. Polyt. J., ccii, 434—446).

THE author gives the analyses of the fine and of the sandy parts of good Portland cement, and remarks that the composition approaches to that which a mixture of 2 parts dry hydrate of lime and 1 part clay would give. He then quotes a great number of experiments made by mixing the cement with various acid and saline solutions, instead of water. The most noteworthy of these are those made with the carbonates of soda, potash, and ammonia, which cause the cement to set with great rapidity, and to acquire a hardness so great that it can



hardly be scratched by a knife, and a compactness such that it can be written on, without the ink exhibiting any tendency to run.

C. H. G.

**Note on Steam Boiler Explosions.** By M. MELSENS (Ann. Chim. Phys. [4], xxiv, 218—222).

THE author starts with the supposition that many steam-boiler explosions are caused by the water assuming the spheroidal state, and being suddenly converted into vapour. He finds that the spheroidal state can be, to a great extent, prevented by furnishing a capsule with a number of spikes, which conduct the heat from the capsule to the water, and produce a regular evolution of steam. The production of the spheroidal state is not entirely overcome in this manner; but it is extremely difficult to obtain water in this condition with such an apparatus. The author, therefore, recommends that the interior of steam boilers should be thus furnished.

A. P.

**Means of Protecting Textile Fabrics, &c., from Fire.**

By A. PATERNO (Ann. Chem. Pharm., clxi, 282—284).

THE author reviews several substances which are used for this purpose. Some of them, as sodium tungstate, answer very well, but are objectionable on account of the cost. The author has made numerous experiments with various substances in their power of rendering fabrics non-inflammable. He recommends the following as being quite equal to sodium tungstate. A mixture is made (shortly before required) of 4 parts of borax and 3 parts magnesium sulphate; this is dissolved in 20—30 parts of warm water, and the dry fabric dipped into the solution, wrung out, and dried.

The action seems to be to form an insoluble magnesium borate, which envelopes the fibres and prevents the escape of inflammable gases, thereby stopping the combustion. A second mixture consists of ammonium sulphate and gypsum. These mixtures may be used for such substances as crape, muslin, canvas, wood, and rope.

A. P.

**Preparation of Collodion Paper.** By E. ZETTNOW (Pogg. Ann., cxlv, 310—319).

THE author having found that tissue paper was the best for his purpose, exposed definite weights of the air-dried paper to the action of various mixtures of nitric and sulphuric acids. After the formation of the collodion paper, it was tested by dissolving a known weight in alcohol and ether. The collodions thus obtained were mixed with solution of bromide and iodide of cadmium, and tested photographically. The following is one formula out of several which the author has found to work very satisfactorily:—150 c.c. of nitric acid (sp. gr. 1.363) are mixed with 400 c.c. of sulphuric acid (sp. gr. 1.82); the temperature then rises to 59°, and 12 grams of paper are introduced. After

20 minutes the paper is removed, the temperature having fallen to 47°. In most of the collodion papers which work satisfactorily, the increase in weight on the original paper seems to be about 40 per cent. A series of experiments on tissue papers prepared from different fabrics, was also made, but with one exception little or no difference was found in the results.

A. P.

### Development of Carbon-Photographic Pictures by means of Potassium Permanganate. (Dingl. Polyt. J., ccii, 338.)

SWAN has discovered that affusion with a solution of potassium permanganate, has an extraordinary effect in strengthening the tone of the picture, the permanganate in the process being decomposed by the gelatin, and yielding a precipitate of an oxide of manganese. The colour of this precipitate is olive-brown, inclining to orange. Though this colour may be objectionable, as far as printing is concerned, the plan is of the greatest value in the reproduction of negatives by means of the carbon process.

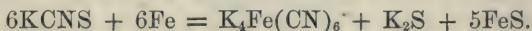
W. S.

### Utilisation of the Waste Substances in Gas Liquor. By R. F. SMITH (Chem. News, xxv, 91).

THE author, after recapitulating the methods by which cyanides have been obtained, gives an analysis of a white mass containing 3 to 19 per cent. of cyanogen for some time produced from leaks near the tuyeres of a furnace at the Portland Iron Works, Kilmarnock. In one specimen, 0.75 per cent. of lithia was found.

Ammonium carbonate and cyanide might be obtained from the vitriol tar of mineral works, while the ammoniacal liquor of gas works might, by using the liquid in a shower, 1 vol. to 18 of gas, be raised from its present strength of 5° Twaddell to 10° or 11°. Much ammonium bicarbonate is often thrown away in the tar of the tanks and condenser. Sal-ammoniac is sometimes deposited in the hydraulic mains. The process usual in Scotland of distilling off the volatile ammonia into sulphuric acid, gives a sulphate of good quality. The Coffey still has not met with much favour.

From the spent water of the ammonia works ammonium sulphocyanate can be procured by evaporation, and might be converted into ferrocyanide by driving off the ammonia with potash, and heating the residue with iron. The reaction occurs thus:—



C. G. S.

### Aniline Oil and Aniline-Black. By CARL HARTMANN (Dingl. Polyt. J., ccii, 389).

THE various kinds of aniline oil, which are used for the manufacture of aniline black, never consist of pure aniline, their composition altering

with the boiling points and specific gravities. These anilines ordinarily consist of from—(a) 60 to 65 per cent. of a product boiling between 180° and 185°, which may be regarded as almost pure aniline. (b) 18 to 22 per cent. of a product boiling from 185° to 192°, which may be considered to be a mixture of aniline and toluidine. (c) 8 per cent. of a product boiling from 192° to 198°, which is toluidine; and (d) 4 to 6 per cent. of other products, as xyldine, cumidine, &c.

The sp. gr. of the above fractions are about as follows:—

(a.)	From 2.75° to 3.4°, Baumé.	
(b.)	„ 1.6° to 2.1° „	Pure aniline of Coupier, 3.5°, Baumé.
(c.)	„ 0.6° to 1° „	Ordinary toluidine, 0.88°, „
(d.)	about 0.5°.	Pseudo-toluidine, 0.50° „

Pure aniline oil of Coupier, as also all products boiling from 180° to 185°, yield beautiful brilliant blacks. Pseudo-toluidine, and the products boiling from 185° to 192°, yielded a black with a blue shade. Ordinary toluidine of Coupier, and the boiling products above 192°, gave unsatisfactory shades between brown and black.

In testing the quality of aniline required for black colours, it will then be necessary to make the following observations:—

1stly. For rapidity of observation, Baumé's areometer is a useful guide. If not wilfully adulterated, aniline oil with a sp. gr. of 2° to 3½° B., yields a black satisfactorily; at more than 3½° B., it generally contains nitro-benzene; and at less than 2° B., it contains too much toluidine, which is decidedly injurious.

2ndly. Fractional distillation gives a still more accurate idea of the value of the oil, the quantity coming over between 180° and 190° being taken as the measure thereof.

3rdly. The author finds that 400 grams is the smallest quantity of pure aniline of Coupier that can be taken to obtain a certain amount of black colour, and knowing this, he tests the value of other aniline oils by a comparative observation of the amount required to produce a proportionate quantity of black dye.

W. S.

### The Colouring of Paper and Leather, &c., with Aniline Lakes. By FERD. SPRINGMÜHL (Dingl. Polyt. J., ccii, 382).

THE author has accidentally discovered that every kind of paper, as also leather, linen cloth, &c., may be coloured to any extent by the use of an alcoholic solution of any aniline colour in a solution of resin. The same resin may be used for this purpose that is recommended by the author in colouring glass and mica (p. 862 of last volume), but an easily soluble lake must be employed, and for equal bulks of alcohol used in dissolving, much less of the resin containing lake must be used in this case.

The colour may be either applied to paper as a paint, or the paper may be soaked in the solution, and hung up to dry.

W. S.



**New Method of Fixing Aniline Colours on Cotton Wool.** By  
M. REIMANN (Dingl. Polyt. J., ccii, 380).

THE author finds that starch possesses the peculiar power of absorbing the colouring matter from solutions of aniline colours, and fixing it upon itself. If a thin paste be made of wheat or potato starch, and cotton wool be soaked therein, and the wool so treated be worked in some aniline-colour bath, a tint is obtained of the required shade.

It is advisable to use also a certain proportion of size, as the shades were found to be obtained by its use more readily than when it is not employed.

W. S.

**Use of Sodium Silicate (Water Glass) in Soap-making.** By  
GUIDO SCHNITZER (Dingl. Polyt. Jour., cciii, 129—132).

IN the ordinary fat soaps, sodium silicate is not of much service, as these are sufficiently hard and durable without this addition; but in the case of palm-oil and cocoa-nut-oil soaps, its presence is of great value, as the alkalinity is hereby raised, and a greater hardness and durability conferred. It is on this account much used in toilette soap manufacture. During the American war, when the price of rosin rose very high, sodium silicate was much used as a substitute in soap making. The richer the silicate employed in the soap mixture is in silica, the more active and durable the soap is found to be.

The author has made a number of experiments, in order to find a mixture which on fusing will yield a silicate as rich as possible in silica, without rendering it insoluble in boiling water. The following mixture yielded on fusion the best silicate for the above purposes:—

100 parts soda-ash, with 180 of sand, in which the soda-ash contains 91 per cent. of  $\text{Na}_2\text{CO}_3$ . In the solution of silicate obtained on treatment with boiling water, the proportion of the  $\text{Na}_2\text{O}$  to the  $\text{SiO}_2$  would then be as 1 : 2.9.

After long boiling with water, there ordinarily remains a slimy residue, which, on boiling up with fresh dilute soda-ley for a long time, furnishes a concentrated solution of silicate. This residue, consisting of silica with insoluble higher silicates, was boiled with soda-solution of 6° Baumé, and the solution concentrated to 40° B., when the proportion therein of  $\text{Na}_2\text{O}$  to  $\text{SiO}_2$  was found to be as 1 : 1; and on cooling there crystallised out sodium silicate of the formula  $\text{Na}_2\text{SiO}_3 + 8\text{H}_2\text{O}$ , in white foliated crystals.

W. S.

**Miscellanea.**—*Hardening of Hydraulic Magnesian Limestone* (Dingl. Polyt. J., ccii, 386).—*The so-called Swedish Safety-Matches.* By A. KRIWANCK (ibid., 391).—*The Blue Burning of Ultramarine direct from the Raw Moss.* By C. FÜRSTMANN (ibid., 446).—*The Addition of Lead in the Refining of Copper* (ibid., 476).—*Manufacture and Application of Artificial Heavy Spar* (ibid., 478).

# PROCEEDINGS AT THE MEETINGS OF THE CHEMICAL SOCIETY.

Anniversary Meeting, March 30th, 1872.

Dr. Frankland, F.R.S., President, in the Chair.

The following Address was read by the President :—

GENTLEMEN,

We meet to-day on our 31st Anniversary, and it now devolves upon me, on behalf of the Council, to lay before you a statement of our position and prospects.

A retrospect of the progress of the Chemical Society from its foundation to the present time, affords a very gratifying proof of the continually increasing interest with which our science is regarded in this country. In the year 1841, the Chemical Society numbered only 77 members; there are now 656 Fellows, besides Foreign Members, enrolled in its books. To this aggregate increase of the prosperity of the Society, the past year has contributed its full share. Indeed, in no previous year in the Society's history, except that of its birth, has the addition to our numbers been so large as during the past twelve months. Notwithstanding the loss of 17 Fellows from various causes, our list still exhibits the large increase of 42 names.

Number of Fellows (Anniversary) March 30th 1871 .....	582
Since elected and paid admission fees.....	59

641

Withdrawn: Dr. E. Burton Brown, Dr. Frederick Guthrie, George Maule, Esq., William Ritchie, Esq. ....	4
Deceased.....	13

17	17
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Number of Fellows March 30th, 1872 .....	624
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Number of Foreign Members (Anniversary) March 30th,	
1871 .....	34
Deceased: C. J. Fritzsche, Dr. Adolph Strecker ....	2
	<hr/>
Present number of Foreign Members .....	32
	<hr/>
Associate .....	1

Besides the two Foreign Members above named, we have lost 13 Fellows by death since our last anniversary. The names of the Fellows deceased are:—J. S. Abel, Edward Arnold, Dr. John Blyth, J. G. Dale, E. H. Davis, The Rev. Vernon Harcourt, William Hustler, Robert Howard, Sir R. J. Murchison, Bart., F.R.S., E. H. Prentice, A. P. Tarner, Professor A. M. Thomson, and George Whipple.

John Sangster Abel was born in London on the 11th September, 1832. After completing his general education in Germany, he entered the Royal College of Chemistry as student in 1849. In the following year he contributed to the Journal of the Chemical Society a paper conjointly with Mr. H. R. Richmond, "On Bichromate of Ammonia and some of its double salts." In 1851 he became assistant at the College, and continued in that position until May 1853, when he accepted the appointment of chemist for the Mexican and South American Company, and proceeded to Chili. From that period until his decease, he was continually engaged, in that country, in metallurgic pursuits, and in the management of copper and silver smelting works. At the time of his death he was head manager of the smelting establishment of Messrs. Urmeneta and Co., at Tongoy, near Coquimbo, the largest and most important works of this class in South America.

Edward Arnold, of Norwich, was the nephew of Dr. Joseph Arnold, the naturalist and explorer who discovered the *Rafflesia Arnoldi*, a parasitical plant of which a single flower has been known to weigh 13 lbs. The nephew, Edward, entered the retail drug business, in which his success was sufficient to enable him to retire upon a competency after the lapse of 25 years, and he was now able to devote more time to his favourite subjects in chemical and physical science, in which he took much interest. He contributed materially to the organisation and success of the meetings of the British Association and British Pharmaceutical Conference at his native town in the year 1868. Like most busy men, he allowed himself too little relaxation, and thus probably laid the foundation of the disease from which he died on the 5th of January, 1872.



John Blyth, M.D., was born of Scotch parents in Jamaica, in 1814. At an early age he was sent to the South of Scotland for his education, having been first at Bankend School in Caerlaverock, near Dumfries, from whence he was removed to Applegarth Manse, in Dumfriesshire, and placed under the care of the late Dr. Dunbar, minister of the parish of Applegarth. Here he remained during the rest of his schoolboy days.

On leaving Applegarth Manse, Dr. Blyth entered the University of Glasgow, where he remained for three years attending the arts classes, and in 1833 he became a medical student in this University. In 1834 he removed to Edinburgh, and after studying medicine for five years, he graduated there as an M.D. in 1839.

After obtaining his M.D., Dr. Blyth practised his profession for a short time at Yarmouth, but he soon abandoned the practice of medicine, as he himself states, "for the pursuit of chemistry, from a conviction that it is the almost exclusive source to which physiology and sound practical medicine must hereafter look for their further progress."

The special chemical studies of Dr. Blyth were commenced in the laboratory of Professor Graham, and were subsequently carried on in France under Pelouze, Dumas, Peligot, Gay-Lussac, Orfila, and Chevreul.

After spending a year and a-half in the chemical schools of Paris, Dr. Blyth availed himself of the German schools of chemistry, having spent more than two years in constant work in the laboratory of Giessen, then under the direction of Baron Liebig, and was also for some time in Berlin, with Professor Heinrich Rose and Professor Magnus.

In 1845 Dr. Blyth returned to England, and on the application of the Committee of the Royal College of Chemistry, became associated with Dr. Hofmann in that institution. By many of the earlier students of this college, Dr. Blyth's kind manner, patient and laborious exertions, and his clear style of communicating information, must be remembered; and the high appreciation in which he was held by those who availed themselves of the Royal College of Chemistry, was expressed by a testimonial presented to Dr. Blyth on the occasion of his leaving this institution.

In 1847 the Royal Agricultural College of Cirencester offered its chemical professorship to Dr. Blyth. He accepted it, and remained two years.

On leaving this institution, the students, in appreciation of his valuable services and his merits, also presented him with a testimonial in the form of a handsome piece of plate.

In 1849 Dr. Blyth was unanimously elected by the Board of the Queen's College, Ireland, to the Chair of Chemistry in Cork. In this

new institution he had most arduous duties to perform, not only in connection with the Chair of Chemistry, but also in conducting the course of medical jurisprudence. His success as a teacher here was such as to render it necessary to make large additions to the laboratory for the accommodation of the students. Besides filling the chair of chemistry in Queen's College, Cork, Dr. Blyth for many years acted as one of the examiners in chemistry in the Queen's University, an office for which he was eminently qualified, not only from his scientific attainments, but also from his kind and courteous manners.

For several years Dr. Blyth was engaged by the Government in examinations and reports on cases connected with medical jurisprudence in Ireland, and by his services rendered very valuable assistance in matters relating to criminal prosecutions. In matters of this nature there was a cautious pains-taking on the part of Dr. Blyth, and such a thorough knowledge of his subject, that his reports were highly appreciated by those for whom they were undertaken.

The labours of the lecture-room, the laboratory, and his investigations in connection with medical jurisprudence, occupied the whole of his time while in Cork.

These labours were so great as to deprive him not only of leisure for original investigation, but they even prevented him from taking that care of his health which a frame, by nature not robust, required, and his career was materially shortened by almost constant work in the discharge of his many duties. He died of apoplexy on the 24th December last, and was buried near his friend and colleague, Dr. Boole.

Of Dr. Blyth's personal character, all who had the pleasure of his acquaintance, formed a high estimate. He was kind, conciliatory, and honourable on all occasions.

His judgment was greatly relied on by his colleagues and students. For many years Dr. Blyth was a member of the Council of Queen's College, Cork, and exercised great influence in its deliberations. His loss is regarded as a great calamity to the institution to which he belonged; and few men have ever been more beloved during life or more regretted in death than Dr. Blyth.

Dr. Blyth married the second daughter of the late Rev. Dr. Dunbar, of Applegarth. He has left a widow and two sons to mourn his loss.

John Dale, jun., was born at Manchester, on the 13th January, 1840. He received the rudiments of a good education at the Manchester Commercial School, and at the age of 14 went to a school at Mannheim, where he remained for two years. Here he acquired a thorough mastery over the German language, and afterwards spent some time in

visiting the educational and technical establishments of Germany. He acquired a sound technical chemical knowledge, chiefly from his father, whose large experience and great success in chemical technology rendered him the best instructor his son could have had.

He soon became the principal manager of the extensive chemical works of Messrs. Roberts and Dale, situated at Warrington, where the operations were of such a nature as to require much labour, attention, and anxiety. His zeal for this work, however, never flagged, but with an indomitable and energetic mind in a weak and nervous frame, he exerted himself to the utmost to develop and improve the various processes entrusted to his care, and he was very successful. He made several improvements in the fixing of aniline colours upon calico, in the manufacture of oxalic acid from sawdust, and in the preparation of white lead. He was fond of pure as well as applied science, and devoted many of his leisure hours to the microscope.

As their Secretary, the Philosophical Society at Warrington have lost a most active and deservedly esteemed officer.

A few years ago a serious explosion occurred at the works in which he was manager, and, although he was not himself physically injured, his nervous system received a shock from which he never afterwards entirely recovered.

In private life Mr. Dale was highly esteemed as a warm-hearted, generous and sincere friend, always anxious to render any service to those with whom he was associated.

In a letter to Dr. Roscoe, Professor J. P. Cooke, of Harvard College, Cambridge, U.S., thus speaks of him:—"I found him wonderfully intelligent, and remember with great pleasure my short intercourse with him. He was one of the excellent of the earth."

He suffered for many months from a severe cold, and his physical powers became so completely exhausted, that he died at last from weakness on October 16th, 1871. He has left a widow and children to mourn his loss.

E. H. Davis, F.G.S., died on the 9th of February, 1871, in the 26th year of his age. He was drowned in crossing the Ten-mile Creek, Nelson, New Zealand, while out on a geological survey for the Government.

Carl Julius Fritzsche, was born on the 29th of October, 1808, at Neustadt, in Saxony. In this, his native town, there was no gymnasium, and he, consequently, received his early education from private tutors, until his fourteenth year, when he was apprenticed to his uncle, a pharmacist in Dresden for five years. From Dresden, young Fritzsche went to Berlin, where for  $2\frac{1}{2}$  years he superintended a phar-



macentical laboratory. Although the training he thus obtained was by no means a scientific one, it nevertheless qualified him for the post of assistant to Mitscherlich. In this appointment, which he held for  $2\frac{1}{2}$  years, he enjoyed the best opportunities for following the bent of his inclination with regard to experimental science. Mitscherlich always had the greatest sympathy for beginners in science, and I cannot do better than quote Fritzsche's own expressions of thankfulness to his great master whose influence at this time doubtless produced a profound effect upon his future career. He says, "At this period I conceived a great affection for Mitscherlich. To my grave I shall think of him with the deepest gratitude. With a paternal care he guided my occupations, and gave me the necessary facilities for completing my scientific education."

It was probably Mitscherlich's influence which determined Fritzsche, in 1831, to matriculate at the University of Berlin, after he had already attended lectures for a whole year. At the University, he devoted himself to chemistry, mineralogy, zoology, and botany, and his preference seemed at first to go rather in the direction of botany, for we find him, in 1833, taking for the subject of his inaugural dissertation on going up for his degree, "the pollen of plants;" whilst in the following years, 1833 and 1834, his memoirs "on the pollen of plants and pollenin," and "on arylum," point to the same direction of his original train of thought; and it was not until the appearance of his research on the compounds of calcic chloride with potassic acetate and oxalate, that we find him working in a purely chemical field.

In 1834, Fritzsche removed to Russia, and, in 1836, his name appears for the first time in the "*Mémoires des savants étrangers*," published by the Academy at St. Petersburg. Afterwards, all Fritzsche's memoirs appeared in the publications of the Academy, of which he was elected an associate in 1838, an extraordinary member in 1844, and an ordinary member in 1852. During this time he became also a member of many other learned societies, both Russian and foreign. A large proportion of his time was occupied in scientific services directly rendered to the Russian Government. Thus he was a member of the Imperial Commission for the investigation and utilization of the mineral waters of the Caucasus, the analyses of which he personally conducted. He was Chemist to the Medical Department, and Consulting Member of the Medical Council of the Minister of the Interior. He was also a member of many other commissions, such as that on the introduction of the electric light into Russia, the commission entrusted with the building of St. Isaac's Cathedral, &c.

Notwithstanding these onerous official occupations, Fritzsche's activity in the field of research was most praiseworthy. He is the author of more than 60 memoirs, which mostly belong to the domain

of organic chemistry. Amongst these the most remarkable describe his celebrated researches on the derivatives of uric acid; on nitrous and hyponitric anhydrides; on the derivatives of indigo; on harmaline and its congeners; on hydrocarbons, &c. Fritzsche showed that murexide is the ammonia salt of purpuric acid; he demonstrated the decomposition of anthranilic acid into aniline and carbonic anhydride, and he discovered the isomerides of nitrophenol.

In all these investigations, Fritzsche showed himself to be an extraordinarily zealous and skilful observer, whose keen perception, even the most unimportant phenomena could not escape. What had been passed over unnoticed by other observers, served him as a starting point for new discoveries. For this Fritzsche has sometimes, though most unjustly, been censured. Only seldom and exceptionally are even the greatest scientific discoveries the result of *à priori* thought; on the contrary, they much more frequently spring from an accidental observation sharply and correctly appreciated; and it is no uncommon thing to see how the germ of a new discovery passes unnoticed and unexplained under the eyes of a whole series of investigators, until it is at last seized upon by one who brings out its true significance. Such an one was Fritzsche, and this quality it was which led him to the discovery of facts of the highest interest, but which stand isolated, and still await an explanation. To this category belong his discovery of the transformation of anthracene into paranthracene under the influence of sunlight, and a similar transformation of chrysogene. The same quality of mind gave to many of Fritzsche's discoveries the character of singularity and unexpectedness. His observation of the compounds which hydrocarbons form with picric acid and dinitroanthraquinone, and his research on the molecular changes of tin, illustrate this peculiarity.

The untiring energy with which he worked in his laboratory was not unfrequently interrupted by foreign travel. On these journeys he was always on the alert to obtain new forms of apparatus, or to see new processes of manipulation. He frequently visited England, and all who remember his good-humoured face, will recollect with what zeal and earnestness he inquired after something new in each laboratory he entered. His own laboratory was of the most modest description, but five years ago he fitted up and occupied, in conjunction with N. Zinin, the new and spacious chemical laboratory of the St. Petersburg Academy.

Fritzsche's activity never developed itself in the direction of teaching, but instances are known in which he cordially and effectively assisted young chemists in the pursuit of their studies.

His private life was, on the whole, a quiet and happy one, embittered, however, by the loss of two wives. He survived his second

wife fifteen years, and has left a son and daughter. His relations to his colleagues and acquaintances were uniformly of the most friendly kind, and he was universally regarded as a man of amiable character and kind heart, whose aim was always to do good. Up to the year 1869 he enjoyed uninterruptedly the most robust health, but in that year an attack of paralysis transformed him at once into a feeble old man. Although he recovered somewhat, one side remained paralysed, and speech and memory had irreparably suffered. To his friends, who had always known him full of life and good spirits, this sudden change was most painful, and he himself longed for death to free him from such an existence; nevertheless, even in this condition, he for some time continued his researches and finished his investigation on the molecular changes of the metal tin. In the following year he visited his native country in order to seek amongst his relatives for physical and mental relief for his sufferings. His disease, however, continued to make progress, and on the 20th of June, 1871, death relieved him from a life which had become a burthen to him.\*

William Venables Vernon Harcourt was born in June, 1789. After spending five years in the Navy, the profession for which his father had destined him, he was recalled by his natural bias in favour of literary and scientific pursuits, and became a Member of the University of Oxford, and subsequently he was ordained and appointed to a living in the neighbourhood of York.

About the year 1823, Mr. Harcourt became President of the newly-founded "Yorkshire Philosophical Society." Eight years later he bore a principal part in framing the constitution of a Society whose increasing fame and prosperity has in recent years led to the formation of many similar institutions, namely, the British Association for the Advancement of Science. The constituent meeting of this body was held at York, in 1831. For several years Mr. Harcourt served the association as General Secretary, and he was elected its President for the meeting at Birmingham, in 1839. The main subject of his address, delivered on that occasion, was an inquiry into the history of the discovery of the composition of water, and a vindication of the claim of Cavendish to the honour of that discovery.

To the Journal of the Association and the Philosophical Magazine, Mr. Harcourt contributed several papers on questions connected with mineral chemistry.

In 1860 he made a Report to the British Association on the result of some experiments commenced as early as 1834, on the "Effects of long continued Heat, illustrative of Geological Phenomena." The experiment had consisted in placing a number of minerals, and artificial

\* I am indebted to Prof. Butlerow for most of the details in the foregoing sketch.



mixtures suitable for the production of minerals, under the bottom-stone and in the masonry of two blast furnaces then being erected. When the substances thus subjected to heat and pressure were exhumed, in one case after the lapse of 5, in the other of 15 years, it was found that in most instances the gradual changes and displacements had been such as to render it impossible to identify the substances which had been deposited. The formation of sandstone from river sand, and of a translucent blue mineral, consisting of sulphate of lime, silica, and alumina, and thus resembling lapis lazuli; the penetration of a plate of copper by metallic lead at a temperature at which the lead and a neighbouring block of tin had remained unfused, were the most interesting results of this experiment, which, for the sake both of geology and chemistry, is well worthy of being repeated.

At about the same time Mr. Harcourt drew up a report to the Association on another subject in which he felt a deep interest, the reception of scientific evidence in courts of law.

Becoming apprised towards the close of his life of the presence of a uric acid calculus in the bladder, Mr. Harcourt made himself the subject of some careful experiments on the solvent action of large doses of citrate of potash; and finding the method of determining uric acid by its precipitation by hydrochloric acid, given in the text-books, to yield extremely discordant results, he applied himself to the improvement of this method with, it would seem, perfect success.

But Mr. Harcourt's favourite subjects of study during nearly forty years, were the conditions of transparency in glass, and the connexion between the chemical constitution and optical properties of different glasses. In the course of this research, Mr. Harcourt prepared glasses, into the composition of which there entered severally not less than 33 of the elements, and about a year before his death he prepared a glass containing titanous acid, which promises to give, in combination with a lens of terborate of lead, a compound lens which will be perfectly achromatic. During the last ten years of this investigation, Mr. Harcourt enjoyed the invaluable co-operation of Professor G. G. Stokes, by whom a short notice of this research was communicated to the British Association at its last meeting.

Mr. Harcourt preserved to the close of his life that wide-spread interest in many branches of science which was more common, perhaps more possible, in the scientific men of the last generation than in those of the present. And this interest at eighty years of age seemed never abated by the thought that the pursuit was one in which he must soon cease to bear a part. He died at Nuneham Park, near Oxford, in April, 1871.

Robert Howard, the eldest son of Luke Howard, F.R.S., was

born at Plaistow, on the 27th of June, 1801. On leaving school he entered his father's business of a manufacturing chemist, at Stratford, Essex, in which he continued till the time of his death. After his father's retirement from business he became the senior partner. He was elected a Fellow of the Chemical Society in the autumn of 1841, and was one of the founders and original members of the Pharmaceutical Society, in the formation of which he took great interest.

He took an active part in business, and religious and philanthropic objects occupied the chief part of his leisure, and thus, although a constant student of the progress of chemical science, he had little opportunity for original investigation.

His health gave way about two years before his death, which took place at his country residence, at Ashmore, Dorset, on the 2nd of June, 1871. He married on the 20th of April, 1825, Rachel, daughter of Samuel Lloyd, banker, of Birmingham, by whom he had six sons and two daughters.

William Hustler, the son of John Hustler, Esq., of Bradford, Yorkshire, was born there in 1822. He was educated at home till the age of 17, when he became a pupil of the Rev. Derwent Coleridge, at Helstone, Cornwall. On leaving Helstone he studied shipbuilding, first at Southampton, then in the dockyards of Portsmouth and Chatham. As the building of wooden ships about that time fell somewhat into disuse, Mr. Hustler did not pursue it as a profession. He was engaged for some years in the manufacture of coke at Bristol, for the Great Western Railway, and subsequently as manager of the works for supplying Amsterdam with water.

He first turned his attention to a systematic study of chemistry, metallurgy, mineralogy, and analysis, in the latter part of the year 1855, when he went to the School of Mines, in Truro, attending the lectures, and studying diligently in the laboratory for about a year. He then went to the Mining College at Freiberg, in Saxony, where he continued his studies for three sessions.

In August, 1860, he contributed to the "Philosophical Magazine" a translation of a pamphlet by his friend and former instructor, Professor Breithaupt, of Freiberg, on "Thirteen Systems of Crystallisation." For the last nine years of his life he was engaged in managing a tin mine in the North West of Spain.

He had the pleasure of presenting some specimens of crystals of tin to the British Museum, and was an exhibitor of the products of the mines in Spain, at the Paris International Exhibition, in 1867.

He was himself a successful collector of minerals, of which he had a number of valuable specimens. He died at Orense, in Spain, from an attack of pneumonia, on the 9th April, 1871.

Sir Roderick Impey Murchison, Bart., K.C.B., LL.D., D.C.L., F.R.S., &c., died at his residence in Belgrave Square, on Sunday, October 22nd, 1871, aged nearly eighty years. He was the eldest son of Mr. Kenneth Murchison, of Tarradale, in Ross-shire, and his wife Barbara, a sister of the late Sir Alexander Mackenzie, Bart., of Fairburn. He was born on the 19th of February, 1792, and received the early part of his education at the Grammar School attached to Durham Cathedral. Afterwards he studied for a few months at the University of Edinburgh. In 1807 he obtained a commission in the army, and, in 1808, served in the 36th Foot with the forces in Spain and Portugal under Lord Wellington, afterwards on the staff of his uncle General Sir Alexander Mackenzie, and finally as captain in the 6th Dragoons. He took part in several of the most important battles, carrying the colours of his regiment at Vimiera, and shared in the dangers of the retreat to Corunna under Sir John Moore.

At the conclusion of the war, following out a suggestion of Sir Humphry Davy, he turned his attention to the study of physical science. His first contribution to the literature of the branch of science with which his name afterwards became so closely associated, was a paper read by him before the Geological Society in 1825, on the "Geological Formation of the North-west Extremity of Sussex and the adjoining parts of Hampshire and Surrey." In 1826 he was elected a Fellow of the Royal Society. After some years of investigation at home and abroad, Mr. Murchison published the conclusions at which he had arrived concerning what he designated the Silurian system; for which he afterwards received the Copley medal of the Royal Society.

In 1846, with M. Verneuil, he commenced a geological survey of the Russian Empire, under the countenance of the Imperial Government. Upon presenting his first report, the Emperor Nicholas bestowed on him a decoration and a colossal vase of Siberian aventurine, mounted on a porphyry column, and, three years afterwards, on the completion of the survey, conferred upon him the grand cross of the order of St. Stanislaus.

In 1854, Mr. Murchison published his best-known work, "Siluria; or, the History of the oldest-known Rocks containing Organic Remains, with a brief sketch of the Distribution of Gold upon the Earth." This reminds us that, although the discovery of gold in Australia was practically effected by others, the presence of the precious metal in the mountain ranges of that continent was previously inferred by Sir Roderick Murchison, from their similarity to the Ural Mountains. In his address as President of the Geological Society, in 1844, he predicted the discovery of gold in Australia; and, in 1846, six years before that metal was practically worked there, he addressed a letter to the President of the Royal Geological Society of Cornwall, inciting



the unemployed Cornish tin-miners to emigrate and dig for gold in Australia.

Sir Roderick, having acted for five years as Secretary of the Geological Society, became its President in 1831-2, and again in 1842-3. He assisted in the formation of the British Association, acting for several years, and presiding over its meeting at Southampton in 1846. In 1844 he was elected President of the Royal Geographical Society—a post which he held with a few intervals until recently, when he was succeeded by Sir Henry Rawlinson. The persistency with which he has advocated the necessity of sending assistance to Dr. Livingstone, and the faith that he has evinced in the safety of that traveller are too well known to need more than mention here.

In 1855 he succeeded Sir Henry de la Beche as Director of the Museum of Practical Geology. He was also a Trustee of the British Museum and Director-General of the Geological Survey of the United Kingdom.

In 1863 he was nominated K.C.B., and created a baronet in 1866. From the Universities of Oxford, Cambridge, and Dublin, and nearly all the learned societies of the Continent, he received recognition of his services to science.

Sir Roderick Murchison married in 1815 a daughter of the late General Hugonin, who died in 1869 without issue; the title becomes extinct. In the year 1870, Sir Roderick was seized with loss of speech and difficulty of swallowing, which symptoms, however, gradually abated. On the Thursday previous to his death he caught cold while taking a drive, which brought on bronchitis, under which he sank.\*

Edward Henry Prentice, who met his death in one of the gun-cotton explosions which occurred at Stowmarket, in Suffolk, on the 11th August, 1871, was born at that place on the 25th July, 1838. He completed his general education at Mill Hill Grammar School, and afterwards studied chemistry under Dr. Richardson, of Newcastle, and at the Royal Agricultural College, Cirencester, under Dr. Volcker. At the age of 24 he became partner in an old-established corn and malting business at Stowmarket, in connection with which were works for the manufacture of sulphuric acid and superphosphate of lime. The increase of this branch of the business led to its establishment as a separate concern in 1868, when Mr. Edward Prentice became its manager, in which capacity he continued, up to his death, to devote himself, with great zeal and success, to the development and improvement of the special branches of manufacture in which he was interested. Mr. Prentice also undertook the manufacture of strong

\* The biographical sketch of Sir Roderick Murchison is taken from the *Pharmaceutical Journal*.

and pure nitric and sulphuric acids for the gun-cotton factory which was established by the Messrs. Prentice in 1864, and he was thus led to be of important assistance, in developing the manufacture of that material, to his brother, Mr. Eustace Prentice, the manager of the gun-cotton works. It was during the temporary absence of the latter that Mr. Edward Prentice encountered his fearfully sudden death, along with his nephew Mr. William Kirby Prentice, while labouring most courageously to rescue human life.

Mr. Edward Prentice possessed great energy and zeal, the operation of which extended to other matters than mere business. Thus he took a very active part, together with Sunday school teachers and others at Stowmarket, in promoting the advancement of knowledge among the humbler members of his community.

Adolph Strecker was born on the 21st October, 1822, at Darmstadt, and was the fourth son of Ludwig Strecker, an officer attached to the Grand Ducal Court. He attended the Gymnasium of his native town for eight years, from which, having reached the highest class, he was transferred, in April, 1838, to the higher Gewerbeschule, where he remained  $2\frac{1}{2}$  years. At Easter, 1840, he passed with credit his matriculation examination, and entered the University of Giessen as a student of natural science in the autumn of the same year. He devoted himself chiefly to chemistry, for which, as a boy, he had already shown great predilection. He remained at Giessen until the end of the summer session of 1842, working in Liebig's laboratory, and attending the lectures of Liebig, Kopp, Buff, and Knapp.

Not yet 20 years of age, Strecker took the degree of Doctor of Philosophy at Giessen in August, 1842, and was immediately afterwards appointed teacher in the Realschule at Darmstadt, where, in addition to mineral and organic chemistry, he had to deliver courses of lectures on physics, mathematics, botany, and mineralogy.

In March, 1846, he had the gratification to receive from Liebig the offer of the Private Assistantship in the Giessen Chemical Laboratory, which he accepted, and from that time devoted himself, under these favourable auspices, exclusively to chemical research, with a zeal, originality, and success which have engraven his name for all time in the annals of experimental science.

Strecker remained at Giessen until the autumn of 1850, and it was during the latter part of his sojourn there that I enjoyed the privilege of his acquaintance and friendship. Working in the same laboratory and upon a kindred subject, I had many opportunities of admiring the enthusiasm, the fertility of resource and conception, and the consummate experimental skill with which he from day to day pursued his researches, whilst his unvaried good humour and high

spirits rendered him one of the most agreeable laboratory companions I have known.

During the period of his residence in Giessen he published the results of many important researches in the "*Annalen der Chemie und Pharmacie*," of which journal he was for many years a most active co-editor. One of the first of these papers appeared in the year 1846; it contained new determinations of the atomic weights of silver and carbon. This was rapidly followed by accounts of his investigations on the reactions of lactic acid; on the separation of cobalt from manganese; on the decomposition of hippuric acid by nitric acid and nitric oxide; on conjugate compounds; on the acids of lichens, and on the lichen colouring matters; on the action of nitric oxide on glycol; on the separation of nickel and cobalt from manganese; and, lastly, his truly classical researches on bile, worthily crowned this series of investigations, occupying but little more than two years of his life.

Passing on to the years 1849 and 1850, the extraordinary activity and success of the young investigator is illustrated by the mention of the following, among numerous other researches which he published in these years:—On styrene and styracin; on tyrosin; on nitromannite and phloridzin; on the artificial formation of lactic acid and alanin; on the preparation and analysis of the ashes of plants—a memoir in which his results brought him to some extent into antagonism with Heinrich Rose, and which might fairly serve as a model of that courtesy and zeal for the truth which ought to distinguish controversies about matters which admit of being weighed and measured. In the same period we have also his investigation, made conjointly with J. Wolff, on the colouring matter of madder, which, taken in connection with Strecker's own subsequent investigation of alizarin, must be regarded as the first link in a long chain of discoveries, terminating in the splendid result of Graebe, Perkin, and Liebermann—the artificial production of alizarin, a result which promises to effect for the cotton industry as great a revolution as that caused in the woollen and silk trades by the discovery of the aniline colours.

In July, 1851, Strecker was appointed Professor of Chemistry in the University of Christiania, and he held this appointment for nine years. His talent for the acquisition of languages soon enabled him to give his lectures in Norsk, and, this accomplished, he lost no time in returning with redoubled energy to his favourite pursuits. During his residence in Norway some of his most valuable work was executed; amongst others, the following memoirs will serve to illustrate both his untiring activity and the great variety of chemical subjects which attracted his attention:—The artificial production of taurin; on the compounds of mercury with ethyl and methyl; on lactic and benzo-lactic acids; on propionic acid; on hydrocyanaldin; on the decom-



position of brucine by nitric acid; and on gallotannic acid, whose glycoside nature he was the first to demonstrate.

These were some of the results of Strecker's researches during the first half of his residence at Christiania; during the second half, that is to say from 1856 to 1860, he gave to the world results of investigations no less numerous and important, amongst which may be mentioned the following:—On sarcine, a new base contained in the juice of flesh; on acetamide; on the identity of nitrosalicylic acid and anilotic acid; on the composition of stibethyl-compounds and of organo-metallic radicals containing tin; on the transformation of paralactic into lactic acid; on the behaviour of piperine with potash; on arbutin and its compounds; on the transformation of guanine into xanthine; and on the decomposition of alloxan by the action of the cyanides.

These brilliant results in the field of research excited, as might be anticipated, the greatest admiration in his native country and elsewhere, and on the vacation of various chemical chairs, attempts were continually made to attract him from his northern home; but he turned a deaf ear to the flattering offers of the chemical chairs in the Universities of Zürich, Greifswald, and Ghent; indeed, he felt very happy in his Scandinavian circle of friends, expressing to me, when I met him at the Paris International Exhibition of 1855, the greatest admiration of Norway, and of the genial but earnest character of the Norwegians. About this time the King of Norway conferred upon him the Order of St. Olaf.

Strecker appeared at this time to have decided upon making Christiania his permanent home, but this resolution was shaken in 1860 by the death of Christian Gmelin, Professor of Chemistry in the University of Tübingen. He was induced to accept this chair and to leave Christiania, notwithstanding that a deputation from the Storting urged him to stay. The high estimation in which Strecker was held in Norway is testified by a marble bust, erected in the University of Christiania, to commemorate the beneficial impulse which he gave to experimental science during his sojourn in that country.

Installed in his new appointment, Strecker's inextinguishable love of research allowed him not a moment of idleness. Experimental work recommenced at once, and memoir after memoir testified to his continued originality and success. Amongst these must be mentioned his comprehensive investigation of a new class of organic compounds, including azobenzoic acid, hydrazobenzoic acid, and azo-ranisic acid; on alloxan; on the composition of the base derived from hydrocyanic acid and aldehyde-ammonia; on valeral-ammonia; on the behaviour of piperic acid with potassic hydrate; on the relations existing between guanine, xanthine, theobromine, caffeine, and caffeidine; on the transformation of parabanic acid into cholestrophane; on the synthesis of glycocetyamine.

In the year 1865 he undertook an investigation which probably led to his early death: the triad compounds of thallium attracted his attention, and the subject was pursued by him with his usual zeal and energy. He exposed himself for a lengthened period to the poisonous influence of the compounds of this metal, the consequence being most disastrous to his previously robust constitution; he became seriously ill, and was only slowly restored to comparative health by a residence at Schwalbach and on the sea coast.

During his occupation of the Tübingen chair, the Emperor of Russia conferred upon him the Order of St. Anne, third class.

On the death of Scherer in 1869, Strecker was invited to succeed him in the Chair of Chemistry at the University of Würzburg. He accepted the invitation, and in April, 1870, took possession of the magnificent professorial residence and chemical laboratory just erected by the Bavarian Government; alas! only too soon to leave it for his grave.

Scarcely had Strecker established himself in his new sphere when the war with France broke up the occupations of the session; the students hastened to join their respective corps, and both Strecker's assistants were instantly transformed into officers of the German Army. The lecture-rooms and working tables were deserted.

The war over, Strecker entered joyously upon the duties—to him pleasures—of his last session, and again a series of papers in Liebig's *Annalen* testified to the activity of research in his laboratory. The following autumn vacation he spent in Berchtesgaden, from whence he returned in September, suffering, though slightly, from the illness which was soon to terminate in death. After a last visit to his native town, he spent the evening of the 27th of October in his usual manner, and in good spirits, with his circle of friends; but a few days later he was laid upon his sick bed, to be released only by death on the 7th of November.

The 9th of the same month he had fixed as the day for commencing his course of lectures. At the hour appointed for his opening lecture he was carried to his last resting place, his coffin surmounted with a chaplet of laurel sent as a greeting from his Munich friends, Liebig, Erlenmeyer, Volhard, and Lehmann. His early death will be long mourned, not only by those who knew him as a warm-hearted friend, but by all interested in the progress of chemical discovery.

Strecker was twice married—in 1852 to Miss Weber of Darmstadt, who died in little more than a year, after giving birth to a daughter; and in 1855 to his cousin, Miss Lina Strecker, of Mainz, whom he has left a widow with two daughters and a son.\*

\* For the greater part of this biographical sketch I am indebted to Professor Rudolph Wagner, of Würzburg.

Alfred Phythian Turner was one of the younger Fellows of the Chemical Society. He gave promise of being a successful analytical chemist, but suffered much from ill health, and was induced to seek in Australia a more genial climate than that of his own country. He returned a short time since in a very weak condition, and soon afterwards died.

Alexander Morrison Thomson was born in London on the 4th of February, 1841. The earlier years of his life were passed at Aberdeen, whither he had been removed to receive his education; and, among other distinctions, he obtained a first prize in chemistry at the University there. Returning to London in 1859 he became a student at King's College, and matriculated at the University in the following year, his knowledge of experimental science giving him the leading position at both places. He graduated B.A., with prize in chemistry and other "honours," in 1862; in 1863 he obtained the exhibition in chemistry and natural philosophy with further honours, and passed the 2nd B.Sc. examination in 1864, when he reached the first place in chemical and geological honours. He took the degree of D.Sc. in 1866, the subject of examination being organic chemistry. Much of the knowledge necessary for these science degrees was acquired at the School of Mines in Jermyn Street, where Thomson studied mineralogy, geology, and chemistry.

It will hardly be credited that so brilliant a university career was mainly the fruit of the utilisation of a few spare hours remaining out of the day when business was over, but such was actually the case. Nor did such varied and eminent attainments, such intense power of application, have long to wait for their reward. He was at once selected by Sir Roderick I. Murchison to proceed to Sydney University, New South Wales, where he was appointed reader in mineralogy and geology, with a chemical tutorship attached; and in 1870 he became professor of the two former subjects. This reward he had richly merited by a geological survey, during the two previous years, of the county of Argyle: a full account of it was published by the Royal Society of Sydney, of which he was a member. At the instance of the Government he visited the Wellington caves, on the Abercrombie River, which have become famous for their extraordinary richness in peculiar mammal remains, and drew up a valuable report, which was published by the commissioning authority. His last memoir, "On the Diamond Fields of Mudgee," was a clear inductive summary of the circumstances under which the diamond actually occurs at that place and generally, and it contained predictions, based on these data, for other localities. He records his fruitless endeavour to throw light on the vexed question as to the primitive matrix of the diamond.



Thomson was always ready to impart scientific knowledge, whether within or without the sphere of his immediate duties. While he charmed his students by his pleasing manner and fertility of intellectual resource, he was gaining high encomiums from outsiders by expository lectures and written articles; but—rare accomplishment!—he always remembered that the popular style should be but a vesture of the scientific spirit. His little work on elementary mineralogy is a singular example of his achievements in this respect, and was widely appreciated.

The work of investigating the Wellington caves had been arduous and perilous from the first. But Thomson shrank from neither toil nor danger; and, in the course of his long underground labours, his chest became affected. From that time he gradually sank, and on November the 16th, 1871, died of heart disease and dropsy, at the early age of 30 years. His remains were attended to their resting-place by the entire University.

Personally, Thomson was very much beloved; indeed his self-forgetfulness and zeal were sure to endear him to many. In Sydney he was universally known and esteemed. In him the Society will regret to have lost a distant and honoured representative; and a large circle of friends will lament that so much learning, so noble a disposition, and such measureless activity should have been cut down before the harvest.

George Whipple, who died on October 31st, 1871, was one of the earliest supporters of the Chemical Society, and for many years a constant attendant at its meetings. Engaged daily in the City of London in the manufacture of many of the chemical substances employed by pharmacists, and in the analytical examination of drugs, he had frequent opportunities of observing new facts. These he seized intelligently, and elaborated patiently; the results are recorded in papers communicated chiefly to the "Journal of the Pharmaceutical Society." He retired from active life 13 years before his death.

The prosperity of a Society like ours cannot be completely gauged by the annual increase of its members. To quote the words of one of my predecessors in this chair, "the task of the Chemical Society is the promotion, by earnest research, of the science of chemistry. To form an adequate estimate of our vitality, we have, therefore, not only to consider the expansion of our list of members, but also, and indeed chiefly, the influence which our united efforts have exercised upon the advancement of experimental science, *i.e.*, the number and value of the papers which we have been able to collect."

Contemplated from this point of view, the progress of the Society during the past quarter of a century has been of a somewhat chequered

character. From 1848 to 1851 the number of papers annually presented to the Society gradually rose to 40; the inflow of the records of new researches then rapidly diminished, until in the session 1855-56 only 10 papers were received, although in the meantime the number of Fellows had augmented from 229 to 256. It was not until the session 1862-63 that the original communications to the Society again reached 40, the number of Fellows having in the interval increased to 397. It is remarkable that these two years of unusual chemical activity coincide with the years of the two International Exhibitions held in this country.

It is the session of 1866-67, however, which is distinguished as that of maximum activity, the number of papers read in the twelve months preceding the 31st of March, 1867, having been no less than 54, the roll of Fellows having 499 names. From that period to the present the number of Fellows has steadily increased, whilst the number of original communications made to the Society has gradually diminished down to 22—the number of papers presented to the Society during the year ending this day.

The following is a list of the papers read at the meetings of the Chemical Society from March 31st, 1871, to March 30th, 1872.

- I. "On Burnt Iron and Burnt Steel": by W. Mattieu Williams.
- II. "On the Formation of Sulpho-acids": by Henry E. Armstrong.
- III. "On a Water from the Coal Measures of Westville, Nova Scotia": by Professor How.
- IV. "On some Saline Compounds of Cane Sugar": by C. Haughton Gill.
- V. "On a New Double Salt of Thallium": by R. J. Friswell.
- VI. "On the Action of Nitric Acid on Dichlorophenol Sulphuric Acid": by Henry E. Armstrong.
- VII. "On a Process for the Estimation of Fluorine": by Archibald Liversidge.
- VIII. "On Anthraflavic Acid": by W. H. Perkin.
- IX. "On the Distillation of Wood": by Watson Smith.
- X. "On Burnt Iron and Steel": by W. H. Johnson.
- XI. "On an Improved Syphon": by F. Hart.
- XII. "On Essential Oils—Part II": by J. H. Gladstone.
- XIII. "Observations on Nitrochlorophenols": by Henry E. Armstrong.
- XIV. "On Eulyte and Dyslyte": by H. Bassett.
- XV. "On the Nitration-products of Dichlorosulphonic Acids—No. IV": by Henry E. Armstrong.

- XVI. "On Quinicine": by D. Howard.
- XVII. "On the Crystalline Principle of Barbadoes Aloes": by W. A. Tilden.
- XVIII. "On the Relation between the Atomic Hypothesis and the Condensed Symbolic Expression of Chemical Facts and Changes known as Dissected (Structural) Formulæ": by C. R. A. Wright.
- XIX. "On Compounds of Tungsten": by H. E. Roscoe.
- XX. "On the Reduction of Ethylic Oxalate by Sodium Amalgam": by H. Debus.
- XXI. "On Metastannic Acid, and the Detection and Estimation of Tin": by A. H. Allen.
- XXII. "On the Quantity of Cæsium contained in the Water of the Hot Spring found in Wheal Clifford": by Col. Philip Yorke.

Notwithstanding the comparatively small number of these communications, we cannot but congratulate ourselves on the great interest and importance attaching to many of them; a study of the foregoing catalogue will demonstrate that, however intense may be the prevailing epidemic of chemical lethargy, some of our Fellows give the most convincing proofs that they, at least, have entirely escaped the infection.

The following three discourses have been delivered at the meetings of the Society, and the large attendance on each occasion testified to the interest taken by our Fellows in the subjects treated of:—

1. "On the Productive Powers of Soils in relation to the Loss of Plant-food by Drainage," by Dr. Voelcker, F.R.S.
2. "On Ozone," by Dr. H. Debus, F.R.S.
3. "An Experimental Inquiry as to the Action of Electricity upon Oxygen," by Sir B. C. Brodie, Bart., F.R.S.

A careful review of the condition of chemical research in this country during the past quarter of a century, as illustrated by the papers read before our Society, shows that with considerable, and in some cases violent fluctuations, the activity of chemical discovery has decidedly diminished. It further demonstrates that whilst the number of persons interested in chemical science has greatly increased, as evidenced by the augmentation in the number of our Fellows from 208 in 1848 to 624 in 1872, the number of researches communicated to the Society has undergone a marked diminution. Thus in the five years ending March, 1848–49–50–51 and 52 respectively, the papers read before us numbered 39, 38, 39, 40, and 34; whilst in the five years ending March, 1868, 1869, 1870–71 and 72 respectively, the number of original communi-



cations sent to the Society was 48, 31, 35, 32, and 22. Hence in the five years ending March, 1852, the aggregate number of original researches laid before the Society was 190, whilst in the five years ending March, 1872, it was only 168.

This lack of progress in discovery cannot be attributed to the continually increasing difficulty of chemical research, because the progress of original investigation elsewhere exhibits extraordinary activity. Take, for example, the evidence of this afforded by the German Chemical Society, which, in 1870, numbered only 463 members, exclusive of foreign members, and yet received no less than 235 original papers. In 1871 this Society numbered 528 native members, and received the results of 238 original researches.

Such being then the great activity in chemical research in Germany, notwithstanding the adverse influences of a gigantic war, it is evident that our own comparative lethargy cannot be accounted for by any greater obstacles which now beset the progress of the interrogator of nature from the known to the unknown. In my opinion several very obvious causes operate to produce a result which, as members of this Society, we must all deplore. I will, on the present occasion, content myself with mentioning only one, which, however, appears to me to carry the chief responsibility in this matter: I allude to the non-recognition of experimental research by our universities. The highest degrees, nay even honours, in experimental science, are bestowed without any proof being required that the candidate possesses the capacity to conduct an original experimental investigation, or that he is competent to extend the boundaries of his science. On the other hand, in all the Prussian universities, and in the best German universities generally, no candidate for a scientific degree is even admitted to examination, unless he has first submitted to the Senate a memoir or dissertation on some original experimental investigation conducted by himself. To be accepted, this investigation must bring to light results of sufficient interest and importance, and more candidates are rejected on the ground of insufficiency of dissertation, than through failure to pass the subsequent examinations.

The entire ignoring of research, in the granting of degrees in this country, not only effectually prevents the training of pupils in experimental investigation, and the consequent actual performance of researches by students; but it has also the effect of withdrawing the attention of teachers of experimental science from original research. Our teachers are not called upon, as in Germany, to devise suitable subjects for research to be pursued by their students; and thus, their attention is not only diverted from this highest and most important field of experimental science, but they feel that to devote any considerable portion of their own time to it would be, to that extent, to

neglect their class duties; inasmuch as their students, in order to pass the examinations prescribed for them, require to be trained in subjects which are foreign to research.

This attitude of our universities towards original investigation is inflicting grievous injury on experimental science, and it is therefore greatly to be desired that the regulations under which degrees in science are granted should, without delay, receive the earnest consideration of the governing bodies, so that experimental research may be rescued from the condition of national disgrace into which it is rapidly drifting.

Whilst the Society cannot but deeply lament this comparative inactivity in original research, there is another of its functions respecting which we can only entertain feelings of unqualified satisfaction. I allude to the publishing duties which it has undertaken. In the early years of our existence, that is to say, between the years 1841 and 1848, the papers communicated to the Society appeared at irregular intervals. In the year 1848, our publications for the first time assumed the shape of a quarterly journal. A further great advance was made in 1861, when the quarterly journal was transformed into a monthly one, whilst its scope was enlarged so as to enable us to publish, not only the papers read before the Society, but also very full abstracts of all valuable chemical memoirs dispersed through the Proceedings, and Transactions of the other learned Societies of Great Britain and Ireland, thus making our Journal a kind of *Comptes rendus* of all the work done in chemical science throughout the country. This was an important step; but science is not national, and it was obvious that the idea involved in this change could only receive its complete and satisfactory development by breaking through the national boundaries of these abstracts, and making them cosmopolitan. This transformation, initiated by my predecessor in this chair, has been accomplished since our last anniversary, and for the past twelve months our Journal has recorded monthly the progress of pure and applied chemistry throughout the world.

In carrying out this great work, the thanks of the Council are due to the Committee of Publication, and especially to the Abstractors, whose arduous labours carefully and conscientiously executed have, in a great degree, contributed to the success of an unexampled enterprise of which the Society may be justly proud.

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The Treasurer then made his financial statement, after which the Society proceeded to the election of the Officers and Council for the ensuing year.

The following is a list of the Officers :—

*President.*—E. Frankland, D.C.L., F.R.S.

*Vice-Presidents who have filled the office of President.*—Sir B. C. Brodie, Bart., F.R.S.; Warren De la Rue, Ph.D., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; Lyon Playfair, Ph.D., C.B., F.R.S.; A. W. Williamson, Ph.D., F.R.S.; Colonel P. Yorke, F.R.S.

*Vice-Presidents.*—H. Debus, Ph.D., F.R.S.; H. M. Noad, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; J. Stenhouse, Ph.D., F.R.S.; and W. J. Russell, Ph.D., and Maxwell Simpson, Ph.D., F.R.S., in place of J. H. Gilbert, Ph.D., F.R.S., and T. Redwood, Ph.D., who retire.

*Secretaries.*—A. Vernon Harcourt, M.A., F.R.S., and W. H. Perkin, F.R.S.

*Foreign Secretary.*—Hugo Müller, Ph.D., F.R.S.

*Treasurer.*—F. A. Abel, F.R.S.

*Other members of the Council.*—H. Bassett; A. Dupré, Ph.D.; F. Field, F.R.S.; H. McLeod; H. E. Roscoe, Ph.D., F.R.S.; R. Angus Smith, Ph.D., F.R.S.; A. Voelcker, Ph.D., F.R.S.; and A. Crum Brown, D.Sc.; Dugald Campbell; G. C. Foster, F.R.S.; Hermann Sprengel, Ph.D.; Thomas Stevenson, M.D.; the five last being instead of E. Atkinson, Ph.D.; C. L. Bloxam; M. Holzmann, Ph.D.; E. J. Mills, D.Sc.; and W. J. Russell, Ph.D., who retire.

After the names of the Officers and Council for the ensuing year had been announced from the chair, votes of thanks were proposed to the President, to the Officers and Council, to the Auditors, and to the Editor of the Journal and Abstractors.





## PAPERS READ BEFORE THE CHEMICAL SOCIETY.

## XI.—On the Action of Sodium-amalgam on an Alcoholic Solution of Ethylic Oxalate.

By Dr. HENRY DEBUS, F.R.S.

In a paper read before the Chemical Society\* in January, 1866, I called attention to the fact that those organic acids which have been examined with care do not contain in one molecule more water residues (HO) than carbon atoms, and that in this respect they resemble the alcohols. Before, however, it is possible to accept this fact as a rule for all organic acids, it is necessary to show that the formulæ of those bodies, which are said to contain more radicals HO than carbon atoms have not been correctly determined. Amongst the latter is one which, in many respects, deserves the attention of chemists. I allude to glycolinic acid, discovered and described by Friedländer in the year 1864. The sodium salt of this substance is formed by the action of sodium-amalgam on an alcoholic solution of ethylic oxalate, and is distinguished from sodic oxalate by containing three atoms of hydrogen more and one atom of sodium less in one molecule than the former does. The formula of the acid is accordingly  $C_2H_4O_4 = CH(HO)_2.CO(HO)$ .

We may therefore consider that one of the hydrogen atoms liberated by sodium-amalgam from the alcohol present, together with one of the oxygen atoms of the oxalate, forms hydroxyl, and that this hydroxyl and another atom of hydrogen take the place of the oxygen atom in the molecule of the oxalate. In this way the ether of glycolinic acid might originate. The possibility of such a reaction cannot be denied by *a priori* arguments, although the probability that it should occur appears very small.

Acetic, glycollic, and glycolinic acids are distinguished by the amount of oxygen contained in one molecule of each.

Acetic acid	..	..	..	..	..	$C_2H_4O_2$
Glycolic acid	..	..	..	..	..	$C_2H_4O_3$
Glycolinic acid	..	..	..	..	..	$C_2H_4O_4$

From this composition it would appear that, as we can prepare glycolic from acetic acid, glycolinic acid ought to be formed by similar methods from glycolic acid. But neither by direct oxidation nor by the decomposition of dichloroacetic and dibromoacetic acid in contact with

\* J. Chem. Soc., xix, 17.

bases has the formation of glycolinic acid been hitherto observed. Moreover, chemists who have been engaged with the examination of the products produced by the action of reducing agents on oxalic acid do not mention glycolinic acid or any of its derivatives.

Independently of the general theoretical interest which attaches to glycolinic acid, its remarkable relation to glyoxylic acid deserves particular attention. If we adopt for glyoxylic acid the formula  $C_2H_4O_4$ , as is the custom of some chemists to do, a most interesting case of isomerism presents itself. But if the formula  $C_2H_2O_3$ , which I believe I have proved to be the correct one, is accepted, and at the same time the facility is considered with which glyoxylic acid can be converted into glycollic and oxalic acids, as well as its general readiness to undergo chemical changes, then it appears remarkable that in no reaction in which it takes part the formation of glycolinic acid should have been observed. In order therefore to decide whether the formula  $C_2H_4O_4$  for glycolinic acid is or is not the correct expression of its molecular composition, whether or not it contains three radicals,  $HO$ , combined with two atoms of carbon, and, finally, to offer a contribution to our knowledge of its interesting relations to glycolic, glyoxylic, and oxalic acids, I determined some years ago to prepare Friedländer's acid in larger quantities and subject it to an examination in the directions indicated. However, only within the last year have I found the necessary time for the execution of this investigation.

I will remark at once, that although I observed with great care the conditions prescribed by Friedländer for the preparation of sodic glycolinate, I have not obtained this substance, but I always found in its place considerable quantities of sodic glycollate. This is the same result which was described by A. Eghis, some months ago, in the "Berichte der deutschen chemischen Gesellschaft zu Berlin."\*

Nevertheless I considered it desirable to pursue my researches; for the question, whether sodic glycolinate is formed by the action of sodium-amalgam on an alcoholic solution of oxalic ether, cannot be considered as solved in a satisfactory manner, until several experiments, under different conditions, have been performed, and the products of each experiment submitted to an exhaustive examination. It is in this respect that my research is far more exhaustive than that of Mr. Eghis, who, it appears, made only one experiment. The trouble I took has been rewarded by the discovery of the formation of sodic tartrate by the *direct* action of sodium amalgam on the alcoholic solution of oxalic ether.

364 grams of pure oxalic ether were mixed with three times their weight of pure absolute alcohol, and small quantities of sodium amalgam

\* 1871, p. 580.



added by degrees; after the addition of each portion of the amalgam the mixture was well shaken until the sodium had dissolved, for which operation about five minutes were required. The temperature of the liquid rose slightly, but no gas was given off. As Friedländer prescribes that the mixture is not to be allowed to become warm, it was surrounded by cold water and its temperature never permitted to rise higher than about  $25^{\circ}\text{C}$ . Two signs are given by which the end of the reaction may be known. The first requires the addition of sodium-amalgam, until the whole has assumed the consistency of a thick salve or ointment; the second, until a further addition of amalgam ceases to raise the temperature of the liquid. Neither of these appears to me to be suitable for the purpose. As far as the first is concerned, I will only remark that the ideas of different persons about the consistency of salve may be very different, and that after the addition of a certain quantity of sodium-amalgam a further supply of this reagent does not cause much change in the consistency of the mixture. With respect to the second, I observed in some preliminary experiments that a given quantity of sodium-amalgam raised the temperature of the mixture in the beginning of the experiment to a higher degree than a similar quantity did near the end, and that, even after the decomposition of the oxalic ether was completed, sodium amalgam produced a slight rise of temperature. I therefore in the present experiment treated the oxalic ether with sodium-amalgam until a portion of the mixture, on being boiled with water, yielded a solution of a decided alkaline reaction. For this purpose about 116 grams of sodium were required, after the addition of which the mixture presented an appearance like that prescribed by Mr. Friedländer. It was now allowed to stand for two days and then mixed with from one to two volumes of ethylic ether and a small quantity of water. This treatment produced a grey, greasy precipitate and a clear yellow solution. The latter contained, besides alcohol and ether, only a small quantity of a yellow liquid, which since, according to Friedländer, no glycolinic acid is contained in it, was not further examined. The greasy precipitate was treated with a small quantity of water, and the undissolved portions, consisting of mercury and sodic oxalate, separated from the aqueous solution by means of a filter. The liquid was slightly concentrated on a water-bath. During the evaporation crystals of sodic oxalate separated on the surface. To the mother-liquor of these crystals nearly its volume of alcohol was added, and the whole allowed to remain at rest for some time. The mixture soon separated into two layers, a lower one of oily appearance, consisting chiefly of carbonates and oxalates of sodium, and an upper one in which the expected sodic glycolinate ought to have been present. This layer was carefully separated from the lower one and concentrated on the water-bath. As no more crystals

of sodium oxalate made their appearance during this operation, a second precipitation by alcohol, as performed by Friedländer, was not deemed necessary. In this manner a few ounces of a dark coloured liquid were at last obtained, from which, whilst standing over sulphuric acid, a comparatively large quantity of crystals, the supposed sodic glycolinate, separated. An experiment undertaken with the view of separating the crystals from the alkaline and syrupy mother-liquor, by pressure between layers of filtering paper, did not give a good result. Purification of the salt by recrystallisation from water would evidently have required, on account of the great solubility of sodic glycolinate in this menstrum, a great sacrifice of the precious material, and the use of diluted alcohol in place of water did not appear very promising, because the solubility of sodic glycolinate and the accompanying impurities seemed to be nearly the same in this liquid. As a preliminary experiment had shown that the calcium salts of the acids produced by the action of sodium on oxalic ether crystallise from water with far greater facility than the corresponding sodium compounds, the following method was adopted as best calculated to give pure compounds.

To the mother-liquor containing the supposed sodic glycolinate, diluted alcohol was added until the solution of the crystals had been accomplished, and then, by addition of an alcoholic solution of oxalic acid, the sodium thrown down as sodic oxalate. The filtrate of the latter was freed from alcohol by evaporation on the water-bath, subsequently diluted with water, and neutralised with calcic carbonate. After the removal of the excess of the carbonate by means of a filter, and suitable concentration of the clear solution, the latter was allowed to crystallise. A large crop of papillary crystals soon made their appearance.

It will be remembered that by the addition of alcohol to the original solution of the greasy precipitate, an oily liquid containing, besides carbonate and oxalate of sodium, also the sodium salts of organic acids, had been separated. To this liquid I added an alcoholic solution of oxalic acid, and proceeded to prepare the calcium salts of the acids now in solution by the method just described. The result of this experiment was the production of a proportionately large quantity of crystals of the same papillary appearance as those mentioned in the last experiments. The two descriptions of crystals were, therefore, united, and the same was done with their mother-liquors.

In order to purify these crystals, they were first pressed between layers of linen, and subsequently recrystallised from water. As, however, it was found that a small quantity of an impurity, the presence of which revealed itself by a turbidness caused on addition of plumbic acetate,\* could not be removed by repeated recrystallisation, the

\* Glycolinates are not precipitated by this reagent.

aqueous solution of the whole of the crystals was mixed with plumbic acetate as long as a precipitate was formed, and the lead removed from the filtrate of this precipitate by sulphuretted hydrogen and subsequent filtration.

The solution was now concentrated on the water-bath, and then allowed to stand at ordinary temperatures for some time, when a crop of almost pure crystals separated from it. The same process was twice repeated with the mother-liquor from these crystals, so that in all, three crystallisations took place, and three distinct sets of crystals were obtained. The mother-liquor which remained after the last crystallisation was too small in quantity to serve for further experiments. Each of these crops of crystals was recrystallised from water, and each of the mother-liquors worked as long as crystals could be obtained from it. Thus the original crystals were divided into five distinct portions, and as none of the mother-liquors were lost, one or more of these portions ought to have been calcic glycolinate, if this body was at all present amongst the substances with which I operated. The analysis of the above crystals gave the following results :—

- I. Small colourless crystals of the same appearance as calcic glycolate.\* They were twice recrystallised from water. The mother-liquors of the two crystallisations shall be distinguished as first and second mother-liquors respectively.

0.224 grm. dried at 120° C. gave 0.118 grm. calcic carbonate.

0.23 grm. dried at the same temperature gave 0.212 grm. carbonic acid and 0.067 grm. water.

1.668 grm. of the same salt, dried at ordinary temperature in air, lost at 115° C. 0.49 grm. of water.

- II. Crystals obtained from the first mother-liquor of I.

0.204 grm. dried at 115° C. gave 0.107 grm. calcic carbonate.

1.380 grm. dried at ordinary temperature in air lost at 120° C.

0.406 grm. of water.

The appearance and reactions of this salt agreed with I.

- III. Crystals from the second mother-liquor of I.

0.234 grm. dried at 120° gave 0.121 grm. calcic carbonate.

0.331 grm. dried at ordinary temperatures in air lost at 120° C.

0.097 grm. of water.

- IV. Crystals from the mother-liquor of II.

0.274 grm. dried at 120° gave 0.143 grm. calcic carbonate.

1.249 grm. dried at ordinary temperatures lost at 120° C.

0.368 grm. of water.

\* The aqueous solution gave no precipitates with lime-water, argentic nitrate-plumbic acetate, and mercuric chloride respectively.



V. Crystals left by partially dissolving some of those mentioned under I in water.

0.2515 grm. dried at 120° C. gave 0.131 grm. calcic carbonate.

0.3535 grm. dried at ordinary temperatures in air lost at 120° C. 0.102 grm. of water.

The percentage composition of the salts dried at 120° C. is accordingly.

	I.	II.	III.	IV.	V.
Carbon .....	25.13	—	—	—	—
Hydrogen. ...	3.23	—	—	—	—
Calcium ....	21.07	20.98	20.68	20.87	20.83
Oxygen. ....	—	—	—	—	—

Calculated according to the formula  $\text{Ca}[\text{C}_2\text{H}_3\text{O}_3]_2$ .

Carbon.....	25.26
Hydrogen .....	3.16
Calcium .....	21.05
Oxygen .....	—

The percentage amount of water of the salts dried in air at ordinary temperatures is as follows:—

	I.	II.	III.	IV.	V.
Water .....	29.3	29.4	29.3	29.4	28.8

The formulæ  $\text{Ca}[\text{C}_2\text{H}_3\text{O}_3]_2 + 4\text{H}_2\text{O}$ , and  $2\text{Ca}[\text{C}_2\text{H}_3\text{O}_3]_2 + 9\text{H}_2\text{O}$ , require respectively—

$\text{Ca}[\text{C}_2\text{H}_3\text{O}_3]_2 + 4\text{H}_2\text{O}$ .....	27.48 water.
$2\text{Ca}[\text{C}_2\text{H}_3\text{O}_3]_2 + 9\text{H}_2\text{O}$ .....	29.8 ,,

The amount of water of crystallisation of the salt dried in air has, therefore, been found from .5 to 1 p. c. less than is required by the second formula. The cause of this difference appears to be the facility with which the salt loses water in air more or less dry.

0.572 grm. of the same crop as I, dried over sulphuric acid lost at 120° C. 0.126 grm. of water or 22.0 per cent. The formula  $\text{Ca}[\text{C}_2\text{H}_3\text{O}_3]_2 + 3\text{H}_2\text{O}$  requires 22.1 p. c. This is the same amount of water that I found to be contained in calcic glycolate dried under similar conditions, but prepared from the products formed by the oxidation of ethylic alcohol by nitric acid.\*

a. 6.490 grms. of a solution of salt I, saturated at 10° C., left after evaporation 0.079 grm. residue dried at 120° C.

\* Ann. Chem. Pharm., c, 8.

b. 7·865 grms. of a solution of calcic glycolate, which had been prepared from the oxidation-products of alcohol, and saturated at  $10^{\circ}$  C., left after evaporation 0·096 grm. residue dried at  $120^{\circ}$  C.

Both solutions were made under exactly similar conditions.

Therefore, one part of the salt *a* requires at  $10^{\circ}$  C. 82·1 parts of water, and one part of calcic glycolate at the same temperature 81·9 parts of water for solution. It is, therefore, certain that the salts obtained by the treatment of oxalic ether with sodium amalgam do not contain, after their conversion into calcium compounds and extraction as described in this paper, a trace of the so-called glycolinate of lime, but consist entirely of calcic glycolate. It is impossible, according to Mr. Friedländer's description of calcic glycolinate to have mistaken this salt for the corresponding one of glycolic acid. Glycolinate of calcium contains, according to this gentleman, 53 p. c. of water of crystallisation and has the formula  $\text{Ca}[\text{C}_2\text{H}_3\text{O}_4]_2 + 14\text{H}_2\text{O}$ , whilst none of the salts examined by me were found to contain more than 29·5 p. c. of water. Dry calcic glycolinate cannot contain more than 18 p. c. of calcium, whilst I found never less than 20·6 p. c. of the same metal. From the original mother-liquor of the crude calcic glycolate no more crystals could be obtained by evaporation over sulphuric acid. After all the water had gone, a brown amorphous mass remained, the quantity of which was not inconsiderable if compared with the glycolate already extracted. It was possible that this amorphous residue contained calcic glycolinate, and I therefore determined to subject it to a searching investigation. For this purpose it was redissolved in water, and the aqueous solution mixed with nearly its own volume of alcohol. A light brown precipitate separated. This precipitate I will call A, and the filtrate of it B. After standing two or three days, B deposited crystals which had the appearance of calcic glycolate. In the mother-liquor of these crystals another crystallisation took place after the liquid had been concentrated to a certain extent on the water-bath. The remaining liquid, on being placed for some days over sulphuric acid, gave first a few more crystals, and then a brown amorphous substance of resinous appearance. The crystals of the first and second crystallisation were recrystallised from water, those of the third could not be subjected to the same process on account of their small quantity.

Analysis gave the following results :—

#### VI. Crystals of first crystallisation.

0·1935 grm. dried at  $120^{\circ}$ , gave 0·1005 grm. calcic carbonate.

0·2715 grm. dried in air lost at  $120^{\circ}$  C., 0·078 grm. of water.

#### VII. Crystals of second crystallisation.

0·285 grm. dried at  $120^{\circ}$  C., gave 0·147 grm. calcic carbonate.

0·401 dried in air lost at  $120^{\circ}$  C., 0·116 grm. of water.

VIII. The crystals of the last crystallisation weighed only 0.447 grm. I only give the numbers obtained by their analysis in order to show that they were impure glycolate of calcium, and not glycolinate.

0.340 grm. dried at 120° C., gave 0.165 grm. calcic carbonate.

0.447 grm. dried in air at ordinary temperatures, lost at 120° C., 0.107 grm. of water.

From these data we obtain the following percentage results:—

	VI.	VII.	VIII.
Calcium .....	20.77	20.63	19.1

The formula  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_3)_2$  requires—

Calcium ... ..	21.05
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	VI.	VII.	VIII.
Water of crystallisation ..	28.7	28.92	23.9

Calculated according to formula  $2\text{Ca}(\text{C}_2\text{H}_3\text{O}_3)_2 + 9\text{H}_2\text{O}$ —

Water of crystallisation .....	29.8
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According to these determinations, in conjunction with their crystalline form and chemical reactions, the crystals obtained, as described above, consist of more or less pure calcic glycolate.

As has been already mentioned, the filtrate B left, after the evaporation of the water and alcohol, a brown amorphous mass. The latter contained at least two calcium salts, which furnished insoluble precipitates with plumbic acetate. To the aqueous solution of this amorphous substance small quantities of the last-mentioned reagent were therefore added, as long as a precipitate (C) was thrown down. The precipitate could not, but the solution could contain a salt of glycolinic acid. In order to discover whether such was the case, the precipitate was separated from the liquor by means of a filter, and the liquid freed from lead by the passage of sulphuretted hydrogen, from calcium by addition of oxalic acid, and from acetic acid by careful evaporation. The strongly acid liquid thus obtained was neutralised with calcic carbonate, and the solution of the calcium salts permitted to concentrate slowly *in vacuo*. At no time during this process could the formation of crystals be observed. The amorphous mass which remained at last weighed only a few grams, and was almost completely soluble in alcohol. No better results could be obtained with the alcoholic solution. As it was possible that the substitution of other metals for calcium might produce crystallisable compounds, an aqueous solution was made, and this carefully precipitated with sodic carbonate. The sodium salts thus formed also refused to crystallise, but were



obtained as amorphous masses, which, with the exception of a few grains, were found to be soluble in alcohol. Sodid glycolinate is insoluble in this liquid, according to Mr. Friedländer. Therefore the liquid B cannot have contained a salt of glycolinic acid.

The lead compounds (C), after careful washing, were decomposed by sulphuretted hydrogen, and the filtrate from the plumbic sulphide concentrated first on the water-bath, and subsequently *in vacuo* over sulphuric acid. Neither the acid or acids of this liquid, nor some salts prepared from them, could be made to crystallise, but were always obtained in the amorphous state.

As there was no guarantee of the purity of these substances, and as no glycolinates could occur amongst them, I abandoned their further examination. The precipitate called A consisted of a mixture of substances, which were partly easily and partly sparingly soluble in water. The latter portion contained tartrate of lime, and the only point about which I am doubtful is whether it consisted entirely of this substance, or contained other salts besides. An accident during its examination deprived me of the material. The parts of A which were easily soluble in water were precipitated by plumbic acetate. The precipitate agreed in properties with precipitate C. The filtrate of it was treated with sulphuretted hydrogen, and after the removal of the plumbic sulphide, concentrated, and then left to stand for some time at ordinary temperatures. An abundant crop of crystals of calcic glycolate separated.

IX. 0.202 grms. of these crystals, dried at 120° C., gave 0.106 gm. calcic carbonate.

0.283 gm. dried in air, lost at 120° C., 0.081 gm. of water.

In 100 parts—

	Found.	Calculated.
Calcium . . . . .	20.99	21.05
	Found.	Calculated.
Water of crystallisation . . . .	28.6	29.8

There is, consequently, also in this portion no calcic glycolinate.

According to the methods described, other experiments were made with sodium-amalgam and oxalic éther, and in each case results obtained which agreed substantially with those just described. The objection might be raised, that too much sodium-amalgam had been employed, and that accordingly the reduction of the oxalic ether had gone too far. In order to meet this objection, I determined to make another experiment, and to use this time less amalgam than on former occasions. 140 grms. of ethylic oxalate were mixed with three times their weight of ethylic alcohol, and to this mixture the amalgam was

added with the precautions mentioned in the description of the first experiment. Only this difference was observed, that not sufficient of the amalgam was added to give to a portion of the liquid, after addition of water, an alkaline reaction. The mixture was allowed to stand for two days after the action of the sodium-amalgam had ceased, then diluted with ethylic ether and a little water. In this case, as in the former experiment, the consequence of this treatment was the production of a greasy precipitate and an amber-coloured liquid. The greasy precipitate was treated with a small quantity of water, and the *neutral* solution thus obtained separated from the undissolved sodic oxalate and mercury by means of filtration. The aqueous solution turned acid after two or three days' standing, but did so at once if its temperature was raised to the boiling point. This would indicate the presence of ethylosodic oxalate, a conclusion which I found confirmed as I became better acquainted with the constituents of the solution.

The examination of this solution was conducted according to a method differing from the one used in former experiments. Calcic acetate was added so long as a precipitate, K, was thrown down. No oxalates of sodium could remain in the liquid. The filtrate of K was then precipitated by plumbic acetate, and the lead precipitate separated by filtration. The solution ought now to have contained glycolinates, besides acetates. In order to extract the former, it was concentrated on the water-bath, and allowed to cool gradually. Crystals of the appearance of plumbic glycolate separated. These were now treated with water and sulphuretted hydrogen, and the liberated acid was neutralised by calcic carbonate. The filtrate from the excess of the latter gave crystals which, not only in composition, but also in properties, could not be distinguished from calcic glycolate.

0.320 grm. dried over sulphuric acid, lost at 120° C., 0.067 grm. of water.

0.253 grm. dried at 120° C., gave 0.133 grm. of calcic carbonate.

Consequently 100 parts contain—

	Found.	Calculated.
Water.....	20.91	22.1
Calcium .....	21.02	21.05

The fact that the water of crystallisation is found somewhat too low, is most probably owing to the circumstance that the salt had been left over sulphuric acid for a long time.

The lead salts obtained in this experiment were evidently of the same character as those obtained on former occasions, and as no glycolinate could be mixed with them, they were not further examined.

The precipitate K, caused by calcic acetate in the original solution,

was boiled repeatedly with small quantities of water, and the hot solutions separated from the undissolved portions by filtration. In the course of a few hours small prismatic crystals separated from the filtrates — crystals which agreed in their physical and chemical properties with calcic tartrate. These crystals dissolved sparingly in water and acetic acid, but easily in nitric or hydrochloric acids. Heated on a piece of platinum foil, they emitted an odour like that of burning sugar. Their aqueous solution gave white precipitates with plumbic acetate and argentic nitrate respectively. Some placed in a test-tube, with a few crystals of argentic nitrate and a little ammonia, gave on heating a mirror of silver. Cold concentrated solution of potassic hydrate dissolved them completely, forming a clear solution, from which on heating a gelatinous precipitate separated. This precipitate re-dissolved if the alkaline liquid was permitted to become cold. The solution of the compound in hydrochloric acid was not precipitated at once by ammonia, but after the lapse of some time. (Difference from calcic racemate.)

The quantitative analysis gave the following results:—

0.586 grm. dried in air lost at  $140^{\circ}$  0.103 grm. of water.

0.138 „ gave 0.066 grm. calcic carbonate.

0.352 „ burnt with chromate of lead gave 0.296 grm. of carbonic acid and 0.100 grm. of water.

Therefore the crystals dried at  $140^{\circ}$  C. contain in 100 parts—

	Found.	Calculated. $C_4H_4CaO_6 + H_2O$ .
Carbon .....	22.93	23.30
Hydrogen .....	3.15	2.91
Calcium .....	19.13	19.41

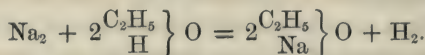
The salt dried in air contains 17.58 p. c. of water, which go off at  $140^{\circ}$  C. According to the formula  $2[C_4H_4CaO_6] + 7H_2O$ , on the assumption that at  $140^{\circ}$  C. 5 molecules of water escape, 17.92 p. c. ought to have been found.

Frisch states that calcic tartrate, dried at  $150^{\circ}$  C., contains only  $\frac{1}{2}$  mol. of water (Supp. to Gmelin, 946). In Gerhardt's, and other books, I find 4 mol. given as water of crystallisation of tartrate of calcium, whilst in the above analysis only  $3\frac{1}{2}$ , or 7 molecules for 2 molecules of the anhydrous tartrate, were obtained. I will only remark that the amount of water of crystallisation is dependent on the conditions under which the crystallisation takes place. Kekulé found calcic racemate, prepared from dibromo-succinic acid, to crystallise only with 3 mol. of water from hot aqueous solutions, whilst it crystallised with 4 mol. from ammoniacal or hydrochloric acid solutions. In other respects I could

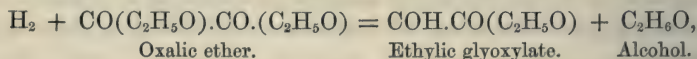


find no difference between the crystals of calcic tartrate prepared from oxalic ether and those derived from other sources.

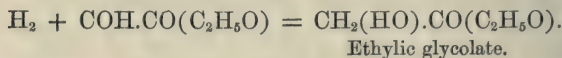
If we now consider the results obtained by the investigation of the action of sodium amalgam on an alcoholic solution of oxalic ether, we perceive salts of glycolic and tartaric acids to be the principal products. The reactions which give birth to these salts may be explained by the following considerations. The sodium of the amalgam separates from the mercury, and forms with alcohol, hydrogen and sodic ethylate—



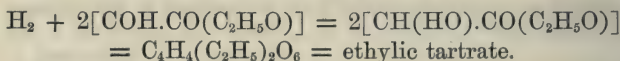
The hydrogen is not liberated, but acts on oxalic ether, as represented in the following equation:—



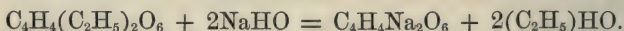
and—



But these two atoms of hydrogen can enter the ethylic glyoxylate one after another. If one only enters, we have an unsaturated molecule of which two can combine and form ethylic tartrate—



On addition of water, sodic hydrate and alcohol are formed from the sodic ethylate. The former decomposes the ethylic tartrate into sodic tartrate and alcohol—



The tartrate is in this reaction not the product of decomposition of a complex molecule, such as desoxalic acid; at all events it cannot be traced to such a molecule, but appears to be directly formed from the oxalate, according to the above explanation. This follows from the following observation. If a quantity of sodium-amalgam be added to an alcoholic solution of oxalic ether not sufficient to decompose the whole of the ether, and afterwards water and a soluble lime salt, a precipitate containing calcic tartrate is at once obtained.

If it be remembered that by simple reactions oxalates can be formed from carbonic acid, we see that a few steps lead us from an inorganic substance of very simple constitution to a complex organic acid. This appears to me to be a point of great interest, because it enlarges our ideas of the formation of vegetable acids in plants.

I am not able to contribute to the history of the other bodies mentioned in this paper. They are salts of acids which are precipitated by plumbic acetate, and remind one by their general properties of the saccharates. I will only mention a few facts which render their formation intelligible. By the action of sodium amalgam on oxalic ether sodic ethylate is most probably produced. The latter, according to Geuther's researches, decomposes oxalic ether into carbonic oxide, carbonic ether, formic ether, and acids of unknown constitution. In my experiments considerable quantities of sodic carbonate were obtained, most likely formed by the decomposition of carbonic ether in the alkaline liquid, but no free carbonic oxide could be observed. If the carbonic oxide met and united with other not saturated molecules, very complex combinations may have been the result.

I cannot conclude without taking notice of a remark made by Mr. Friedländer in the "Berichte der deutschen chemischen Gesellschaft zu Berlin," 1871, page 710. He says that he forwarded to me a specimen of his sodic glycolinate, and that it appeared that I did not perceive any similarity between this salt and sodic glycollate. Mr. Friedländer was good enough to send me in 1866 some of the so-called sodic glycolinate, which consisted of small and partly broken crystals, the whole weighing about *one* centigram. As this salt possesses, according to him, no characteristic reactions, I could do nothing with this specimen, and the whole quantity is still in my possession. Since 1866 I have had no communication with Mr. Friedländer. In 1872, for the first time, did I compare his specimen of sodic glycolinate with sodic glycolate. This comparison was confined to the crystalline form, because the quantity did not permit of experiments. I found a great similarity between the glycolinate of sodium sent to me by Mr. Friedländer and glycolate of sodium prepared by myself.

*Guy's Hospital, April, 1872.*

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# ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

## Physical Chemistry.

**The Meaning of the Atomicity of Elements.** By A. MICHAELIS  
(Deut. Chem. Ges. Ber., v, 48—51).

THIS paper contains suggestions for a mathematical theory of chemical attraction and atomicity. The attraction of an atom for other atoms is supposed to be exerted in certain directions only, or rather to exhibit maxima of intensity in these directions, the number of these maxima being in fact the number of units of atomicity exhibited by the atom. The acceleration imparted by any atom to another atom will therefore be a function, not only of the distance between the two, but also of the direction in space of the line joining their centres.

The exact form of the function with regard to the distance is unknown; but it is probably not negative—that is attractive—for all distances, like gravitation, but positive or repulsive for very small distances. Suppose that the force with which the atoms act upon each other varies, like that of gravitation, according to an inverse power of the distance; then the motion of an atom to or from another regarded as fixed, may be represented by the equation—

$$p = \frac{A}{r^{n+m}} - \frac{A}{r^n}$$

where  $p$  is the acceleration,  $r$  the distance between the atoms,  $n$  and  $m$  any positive whole numbers, and  $A$  a quantity, the value of which is constant for each element [or rather for each pair of elements], but different for different elements. The value of  $p$  is negative or positive according as  $r$  is greater or less than 1. Supposing, then, that for  $r = 1$ , the movable atom has a velocity directed towards the fixed atom; then, since for all values less than 1, the acceleration is positive, this velocity will be gradually diminished, as the movable atom approaches the fixed atom, till it is reduced to 0. The repulsion which then ensues carries the atom beyond the point  $r = 1$ , at which the acceleration again changes sign. In this manner an oscillatory movement is imparted to the movable atom, the amplitude of the vibrations being for the most part restricted within certain limits, but capable, as the author shows by a particular example, of becoming infinite for certain values of the velocity, so that the movable atom then no longer returns to the neighbourhood of the fixed atom, or in other words the combination is broken up.

The smaller attractive forces not in the directions of the maxima are perhaps concerned in the formation of the so-called molecular combinations.

H. W.



**Researches on the Electromotive Force in the Contact of Metals, and on the Modification of that Force by Heat.**

By E. EDLUND (Phil. Mag. [4], xliii, 81—98; 213—226, and 264—278).

THE author in a previous work has pointed out that the discovery of Peltier\* is easily explained if we admit the presence of an electromotive force at the point of contact of the two metals. His researches are now directed towards measuring with great delicacy the electromotive force thus developed, using the principle that the heat developed is a measure of this force.

When a galvanic current passes through a wire composed of two different metals, there are two sources of heat distinct from each other; one due to the resistance of the wire, the other to the production or absorption which ensues at the point of contact of the two metals. For accurately measuring the latter source of heat, the apparatus must be so arranged as to be independent of the former. All foreign influences of temperature must also be eliminated, a difficult condition to fulfil when the apparatus is very sensitive. To ascertain the quantities of heat produced or lost at the surfaces of contact by observation of temperature, it would be necessary to know the calorific capacity of all the metals subjected to examination. This difficulty is sufficiently overcome in the apparatus employed. An air thermometer was so constructed as to fulfil all these conditions. It consists of two perfectly equal cylinders of thin sheet copper, silvered on the outer surface. Into the centres of their circular ends are soldered brass tubes, which admit of the like compound wires under examination being passed into the cylinders, so that their points of contact shall occupy central positions. These cylinders are 125 millims. long and 80 millims. in diameter. They are suitably connected to each other by a glass tube, having an internal diameter of 2·5 millims., in which the index (a mixture of alcohol and water) is placed. The whole is arranged on a mahogany board, which can be tilted slightly from the horizontal position, the angle of inclination being read on a graduated arc. The board also carries a brass scale, divided into millimeters running parallel to the glass tube which connects the two cylinders. To protect the cylinders from variations of temperature from without, they are surrounded by jackets of sheet zinc, having double walls so as to contain water. The sensitiveness of the apparatus was determined, and was found to be  $0\cdot002134^{\circ}\text{C.}$  for one division of the scale. The instrument being thus arranged, the pair of compound wires to be examined were sealed hermetically into their places with a mixture of wax and rosin.

Designating the different metals by A and B, let us suppose that an electric current is passed from A to B in both cylinders; heat will be developed in both equally, and the index will remain motionless. If, however, the current passes from B to A in one cylinder, and from A to B in the other, there will be a development of heat in one cylinder,

\* If a galvanic current be passed through the point of contact of two different metals, that point becomes heated or cooled according to the direction of the current. This discovery is due to Peltier.

and an absorption in the other; and the index will move towards the cylinder in which the cooling takes place.

This movement will cease only when the heating of each cylinder is equal to the cooling occasioned by radiation, and by contact with the surrounding air. In the most perfect of the instruments constructed by the author, the motion of the index ceased after three-quarters of an hour. The difference between the amounts of heat in the one cylinder and the other is therefore equal to the difference between the amounts of heat produced in the two wires. The former difference can be calculated from the displacement of the index.

Theoretical considerations, founded chiefly on the law of Dulong and Petit, give the following equation:—

$$\alpha s = (\sqrt{\beta s^2 + 1}) t,$$

in which  $\alpha$  is proportional to the quantity of heat produced or destroyed at the point of contact at the time of the passage of a current of unit intensity;  $t$  designates the displacement of the index when the current passes from one direction to the other;  $\beta$  is a constant which changes its value when one pair of wires is exchanged for another; and  $s$  represents the current intensity. From this equation is deduced the following:—

$$\beta = \frac{(t_1 s + t s_1) (t_1 s - t s)}{s^2 s_1^2 (t + t_1) (t - t_1)}$$

All observations have been calculated by means of these equations.

From a number of experiments, the details of which are lengthy, the following electromotive series has been deduced, commencing with the most positive, and ending with the most negative metal investigated:—

Iron.	Lead.
Cadmium.	Tin.
Zinc.	Aluminium.
Copper.	Platinum.
Silver.	Palladium.
Gold.	Bismuth.

The compound wires were then subjected to experiment to determine their thermo-electric properties. The following method was adopted:—Near the point of soldering, each wire was bent at a right angle, so that the two wires were parallel, and the distance between them 10 mm. The point of soldering was in the middle of the elbow which united them. The wires thus prepared were passed through a cork into a large test-glass. Through the same cork a very sensitive thermometer was so placed that its cylindrical bulb rested with its middle against the point of soldering. The test-glass was introduced through an aperture in the centre of a thin wooden lid fitted to a large glass vessel filled with cold water. A layer of cotton wool was placed round this vessel as a precaution against changes of temperature from without. The free ends of the wires issuing from the cork in a vertical direction, after passing through the bottom of a small wooden box,

were united to the conducting wires of a magnetometer. The conductivity was then determined in the usual manner for each pair of wires, with some unimportant modifications. From these experiments a thermo-electric series was deduced, and it was found that the metals occurred in the same order as in the electromotive series.

Comparing the electromotive series with the electro-tension series of Volta, Pfaff, Pécelet, and others, no agreement is found; the author concludes, therefore, that "as established by electroscopic experiments, the electric tension series presents no immediate relation with the electromotive forces at the contact of metals; it is impossible, therefore, to determine from that series the amount or the nature of these forces." He considers also that the results of experiment justify him in stating the following propositions:—

"The electromotive force of contact for the eleven metallic combinations investigated, increased with the temperature when the experiments took place at a temperature not exceeding + 30 degrees.

"The thermoelectric forces which at a given difference of temperature arise in different metallic combinations, are not proportional to the electromotive forces of those same metallic combinations.

"If with the aid of the second fundamental principle of the mechanical theory of heat, we calculate the modifications undergone by the electromotive forces of contact in consequence of the increase of temperature, we obtain results which do not agree with experiment."

S. W.

### Measurement of Polarization in a Voltaic Element. By E. BRANLY (Compt. rend., lxxiv, 528).

THE author in these researches proposes to measure, by means of the electrometer, the electromotive force of polarization developed by the positive plate of a voltaic element, when the intensity of the current increases from zero to the maximum obtainable by the element employed. For this purpose he makes use of a common zinc and copper element with dilute sulphuric acid, interposing between the plates two other plates of copper, having a small part only immersed. The difference between the tensions of the zinc and copper, and the tensions of the two intervening plates, which act positively towards the polarised copper plate, give the data required. The electrometer used was a modification of Thomson's instrument. The aluminium needle, with its mirror, was suspended between four sectors connected diagonally, and charged with positive electricity from a pile of two hundred plates of zinc and copper separated by moistened sand. The instrument was found to give constant results when the number of elements in the pile remained the same. The values of the well-known formula—

$$I = \frac{E' - p}{R}$$

were determined, and the results are embodied in the following table:—



I.	E.	E' - p.	p.
1000	1	0.29	0.66
203	1	0.407	0.58
36.5	1	0.64	0.47
17	1	0.97	0.02

S. W.

**On the Absorption Spectra of the Vapours of Sulphur, Selenious Anhydride, and Hypochlorous Anhydride.** By D. GERNEZ (Compt. rend., lxxiv, 803).

IN a previous communication the author has pointed out that the known absorption spectra of coloured vapours consist of groups of fine lines, and can therefore be studied with a greater dispersion than is generally used with coloured liquids. The author in his observations uses a spectroscope of two prisms and a Drummond lime light. To observe the absorption spectrum of sulphur, a porcelain tube about 50 c. in length is taken, furnished with glass ends, and containing some sulphur. At the boiling point of sulphur the tube is filled with vapour, which stops almost the whole of the light, the red end of the spectrum only passing through. If the temperature be greatly increased, so that the vapour is enormously expanded, groups of dark lines are seen furrowing the violet and blue, and extending to the green part of the spectrum. The absorption spectrum of selenious anhydride is more easily obtained, as it appears immediately the substance is volatilised in a tube as above. The groups of lines occur particularly in the violet and blue, and are not seen in the less refrangible portions of the spectrum.

Hypochlorous anhydride in a tube one meter long gives a very satisfactory absorption spectrum; a solution of this gas in water also gives a similar spectrum, which is identical with the spectrum obtained from chlorine peroxide and chlorous anhydride.

A. P.

**Absorption Spectrum of Sulphur.** By G. SALET (Compt. rend., lxxiv, 865).

THIS is a note calling attention to the fact that the author described the absorption spectrum of sulphur in August, 1871, a description of which has again been published by Gernez. To produce this spectrum, the author uses a simple tube of Bohemian glass, closed at the ends, the source of light being a platinum ball heated by a blow-pipe to intense whiteness. The dark bands coincide in position with the bright lines observed when sulphur is volatilised in a hydrogen flame, and both exhibit the maximum intensity at the more refrangible side of the groups. The wave lengths of these maxima are about 477, 470, 465, 458, 454 (millionths of a millimeter).

A. P.

**The Absorption Bands of Chlorophyll.** By L. SCHÖNN (Pogg. Ann., cxlv, 166—167).

REFERS to former publications on this subject in *Zeitsch. für Anal. Chem.*, 1870, and *Pharmaceutische Centralhalle*, 1871, No. 47. The results are not very important.

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*The Spectrum of Hydrogen at Low Pressures.* By G. M. SEABROKE (Chem. News, xxv, 111).

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*Note on the Spectrum of Encke's Comet.* By M. HUGGINS (Proc. Roy. Soc., xx, 45).

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*On Anomalous Dispersion (3rd Memoir).* By A. KUNDT (Pogg. Ann., cxliv, 128—137).

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*Internal Constitution of Gases.* By G. HAUSEMANN (Pogg. Ann., cxliv, 82—109).

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*Method of Determining the Density of a Liquid in a Closed Space.* By F. J. STAMKURT (Pogg. Ann., 470—476).

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*A Simple Thermo-regulator.* By E. REICHERT (Pogg. Ann., cxliv, 467).

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## Inorganic Chemistry.

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**Combustion of Carbon by Oxygen.** By J. DUMAS (Compt. rend., lxxiv, 137—142).

IN two memoirs recently communicated to the Académie des Sciences, Dubrunfaut maintains the four following propositions:—(1.) Carbon dioxide is not decomposed by carbon, without the concurrence of aqueous vapour. (2.) Carbon does not burn in oxygen without the intervention of this same vapour. (3.) A cubic meter of gas, reputed pure and dry, contains 5 grams of water, that is to say 5 milligrams per litre. (4.) This water exists in gases supposed to be dry, in a form which science is unable to determine; it has no appreciable tension.

To test the accuracy of the statement regarding the incombustibility of carbon in perfectly dry oxygen, Dumas selected graphite, as

being the most difficultly combustible of all forms of carbon. Native graphite was purified by fusion with potash, washing with water and boiling dilute hydrochloric acid, and heating to whiteness in chlorine gas (thoroughly dried by passing over pumice soaked in strong sulphuric acid). It was then transferred while still hot into a glass tube which was afterwards exhausted of air, and the combustion was then performed in a stream of oxygen previously dried by passing over potash and sulphuric acid.\*

The experiment showed that the carbon *was completely burned*, 7.0635 grams of it combining with 18.8095 grams of oxygen in producing 25.873 grams of carbon dioxide. These numbers give for the atomic weight of carbon  $C = 6.008$  (if  $H = 1$ ,  $O = 8$ ). Now the volume of carbon dioxide produced in the combustion was 13 litres, corresponding to 13 litres of oxygen consumed. This volume of the gas would, according to Dubrunfaut, contain 65 milligrams of water; and this water, after the alteration of its state, according to Dubrunfaut's assumption, would finally be absorbed by the potash, so that, in estimating the amount of carbon dioxide formed in the combustion; these 65 grams would have to be deducted from the increase of weight in the potash-apparatus. This deduction being made, the atomic weight of carbon deduced from the results of the experiment would be 6.031, a number irreconcilable with all the determinations of the atomic weight of that element.

With regard to the method of drying gases, Dumas adds—(1.) That calcium chloride does not effect complete desiccation. (2.) That potassium hydrate fused and mixed with lime is a very efficient desiccator. (3.) That pumice soaked in sulphuric acid always gives satisfactory results. (4.) That phosphoric anhydride is the most efficient desiccator of all.

Whether gases thus desiccated are absolutely dry it would be difficult to affirm, as there is nothing absolute in nature; but it is certain that any trace of water that may remain in them cannot be detected either by the balance or in any other way.

H. W.

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**Ozone Reactions of the Air in the Neighbourhood of Graduation-houses for Salt Evaporation (Gradirhäusern).** By GORUP-BESANEZ (Ann. Chem. Pharm., clxi, 232—251).

THE author has made a set of experiments on the presence of ozone in the atmosphere, more especially in the neighbourhood of the houses for the evaporation of saline springs. The observations were made with starch and potassium iodide paper, with guaiacum tincture paper, and with thallous oxide paper, the last named of which is turned brown by oxidising agents, and is again bleached by nitrous acid. The behaviour of these test-papers towards ozone, hydrogen peroxide, nitrous acid and ammonium nitrite, was carefully determined. From the determinations of the ozone present in the air close to the evaporation-

\* The oxygen was thereby so thoroughly dried that 50 litres of it passed in a slow stream through a tube containing pumice soaked in sulphuric acid, produced not the slightest increase of weight.



houses, and at a short distance from them, the author has drawn the following conclusions:—

1. That by great evaporation of water, such as takes place at the evaporation-houses, a substance is formed which decomposes potassium iodide, liberating iodine, and also converts thallous oxide into thallic oxide.

2. Such a substance is present in the atmosphere, but in much smaller quantity.

3. That, contrary to what has been formerly stated, ammonium nitrite alone is unable to decompose potassic iodide by liberating iodine, nor can it do so under the influence of carbonic anhydride, nor is it able to change thallous oxide to thallic oxide.

Free nitrous acid occurs in the atmosphere very rarely, but on the evaporation of water, ammonium nitrite and ozone are formed in appreciable quantity, no free nitrous acid being observed. This fact accounted for the large excess of ozone which the author found in the neighbourhood of the evaporation-houses, as compared with the quantity found a short distance away. It was also found that the nearer the test-paper was placed to the evaporating surface, the more intense was the ozone reaction.

A. P.

**Action of Bromine on Phosphorous Chloride.** By M. PRINVAULT (Compt. rend., lxxiv, 868—871).

By the action of bromine on phosphorous chloride, a red-brown substance, crystallising in needles at from  $-4^{\circ}$  to  $-5^{\circ}$ , is obtained. It has the composition  $\text{PCl}_3\text{Br}_8$ , or, as the author thinks it may be written,  $\text{PBr}_5.3\text{ClBr}$ . It can be carefully distilled at about  $90^{\circ}$  without decomposition. Water decomposes it into phosphoric, hydrobromic, and hydriodic acids. It also decomposes when heated above  $90^{\circ}$ , yielding a body of the composition  $\text{PCl}_2\text{Br}_7$ . This substance is very unstable, as by keeping in dry air it splits up into phosphoric bromide and chloride of bromine. It can also be obtained by the direct action of phosphorous chloride on bromine. On allowing the mixture to stand for some time, splendid crystals 2—3 centimeters long are obtained. The latter body, heated with phosphorous chloride, and allowed to cool, deposits yellow crystals of phosphoric bromotetrachloride,  $\text{PCl}_4\text{Br}$ . The author has also been able to obtain another chlorobromide, having the composition  $\text{PCl}_3\text{Br}_4$ . It can be obtained by the direct union of phosphorous chloride with the compound  $\text{PCl}_3\text{Br}_8$ . Most of these bodies can be obtained in a crystalline state, and all of them are at once decomposed by water into phosphoric, hydrochloric, and hydrobromic acids. No body of the formula  $\text{PCl}_3\text{Br}_2$  was obtained.

A. P.

**Barium Chromate.** By EMIL ZETTNOW (Pogg. Ann., cxlv, 167—169).

THE author finds that pure barium chromate dissolves in a boiling solution of chromic acid, and on cooling a salt crystallises out, which on

drying has the appearance of a yellowish-red powder, to which he assigns the formula  $\text{BaO} \cdot 2\text{CrO}_3 = \text{BaCr}_2\text{O}_7$ .

Other experiments were tried, but with the exception of this salt, and  $\text{BaCrO}_4$ , no other barium chromate seems to exist.

M. M. P. M.

**Influence of Saline Solutions, and other Agents, on the Weathering and Decomposition of Felspar.** By H. BIRKER and R. ULBRICHT (Ann. der Landwirthschaft, 1871, 170—182).

IN these experiments 1 kilogram of powdered felspar and  $2\frac{1}{2}$  litres of distilled water were placed in a flask, with the following substances, the amount of dissolved ingredients being determined after the materials had remained together for about  $2\frac{1}{2}$  years.

In the cases in which air or carbonic anhydride was used, the gas was passed to the bottom of the flask at intervals of from 2 to 4 weeks; in the other cases the flasks were made air-tight, and shaken at the same intervals.

The felspar used contained 8.51 per cent.  $\text{K}_2\text{O}$ , 3.37  $\text{Na}_2\text{O}$ , 1.3  $\text{BaO}$ , 16.03  $\text{Al}_2\text{O}_3$ , and 65.52  $\text{SiO}_2$ .

In the following table the quantities of ingredients found in solution are given in grams.

Experiments.	$\text{K}_2\text{O}$ .	$\text{Na}_2\text{O}$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{SO}_3$ .	$\text{SiO}_2$ .
1. Distilled water .....	·051	·078	·058	·006	·044	·049
2. Ditto, with air .....	·037	·064	·044	·005	·044	?
3. Ditto, with $\text{CO}_2$ .....	·071	·114	·076	·004	·046	·069
4. Caustic lime ..... $\frac{1}{10}$ equivalent	·209	·174	·067	·003	·041	·061
5. Calcium carbonate .. 1    "	·042	·073	·112	·009	·040	·019
6. Ditto, with $\text{CO}_2$ .. 1    "	·067	·094	·273	·018	·041	·034
7. Calcium sulphate... $\frac{1}{2}$ "	·053	·074	1.906	·016	2.840	·033
8. Ditto, with $\text{CO}_2$ .. $\frac{1}{2}$ "	·068	·097	1.958	·016	2.684	·062
9. Calcium nitrate .... $\frac{1}{2}$ "	·041	·062	—	·016	·048	·036
10. Ditto, with $\text{CO}_2$ .. $\frac{1}{2}$ "	?	?	—	·017	·048	·045
11. Ammonium sul- phate..... } $\frac{1}{2}$ "	·161	·094	·122	·035	—	·066
12. Ditto, with $\text{CO}_2$ .. $\frac{1}{2}$ "	·162	·107	·147	·015	—	·056
13. Magnesia..... 1    "	·359	·315	·013	·004	·065	·159
14. Ditto, with $\text{CO}_2$ .. 1    "	·312	·255	trace	—	·111	·048
15. Potassium carbonate $\frac{1}{2}$ "	—	—	trace	trace	·048	·026
16. Ditto, with $\text{CO}_2$ .. $\frac{1}{2}$ "	—	—	·029	·007	·040	·029
17. Sodium nitrate .... $\frac{1}{2}$ "	·089	—	·049	·003	·043	·060
18. Ditto, with $\text{CO}_2$ .. $\frac{1}{2}$ "	·096	—	·120	·008	·037	·032
19. Sodium chloride .... $\frac{1}{2}$ "	·163	—	·091	·008	·040	·032
20. Ditto, with $\text{CO}_2$ .. $\frac{1}{2}$ "	·183	—	·123	·006	·034	·057
21. Ferrous hydrate, } $\frac{1}{2}$ " with air..... }	·086	·069	·040	·004	·052	·036

From these numbers it is seen that the action of distilled water with and without air was practically the same. Calcium carbonate, calcium nitrate, with and without carbonic acid, gypsum with and without carbonic acid, potassium carbonate and bicarbonate, and ferrous hydrate, had little more action than water alone. Carbonic acid and calcium

carbonate, with carbonic acid, showed an increased action on the alkalis and silica. In the experiments with lime a much larger quantity of alkalis was dissolved, the lime at the same time entering into combination with the silica. Sulphate of ammonia had an energetic action, more especially on the potash; only in the experiments with this salt and in that with lime, was potash dissolved in larger quantity than soda. In the case of the ammonia sulphate, the base had entered into some combination with the silica, which was not decomposed either by washing until all sulphuric acid was removed, or by heating to  $100^{\circ}\text{C}$ . Eichhorn (*Jahresb. f. Agricultur. Chemie.*, 1859-60, 16) has already shown that silicates, which are decomposed by hydrochloric acid as chabazite, absorb ammonia from its salts. Magnesia acted more energetically than any other agent, seven times more alkalis and three times more silica being dissolved than with water alone. Its somewhat less action in combination with carbonic acid was probably due to the crystallising of bicarbonate on the sides of the vessel.

Sodium nitrate dissolved about double the quantity of potash that water did, but its action was less than that of sodium chloride. These comparative results are in unison with those of Dietrich on basalt (*J. pr. Chem.*, lxxiv, 12, and *Jahresb. f. Agricul. Chemie.*, 1862-63, 14).

E. K.

### The Chemistry of the Devitrification of Glass. By H. E. BENRATH (*Dingl. Polyt. J.* cciii, 19-29).

THE author refers here to the property possessed by glass when repeatedly heated, of becoming crystalline and more or less opaque.

It is noticed that in samples of devitrified or crystalline glass, as compared with the portions of unaltered amorphous glass, slightly more silica is contained, but this excess is insufficient to give any definite information relating to the constitution of the crystals.

The difficulty of obtaining accurate samples of the crystalline glass, *i.e.*, free from any portions of the surrounding matrix of amorphous glass, is very great: hence the difficulty of ascertaining the constitution of the crystalline matter with any degree of certainty.

The author adopts the method advised by Leydholt, in which the crystalline portion of the glass, extracted as carefully as possible, is submitted to partial decomposition under the influence of hydrofluoric acid, and the residue taken for analysis. Hitherto experimenters have come to the conviction that the phenomena of devitrification are due to the fact that certain definite silicates crystallise out slowly in the substance of glass when the latter is kept heated to the temperature at which it softens, or is repeatedly heated. Leydholt has stated that glasses containing more silicic acid than is sufficient to satisfy the formula  $\text{R}_2\text{SiO}_3 \cdot 2\text{SiO}_2$  are, under favourable circumstances, very prone to devitrification.

The author finds, on analysis of the devitrified and transparent amorphous portions of a glass, that their compositions scarcely differ at all; thus in the devitrified portion the percentage composition is  $\text{SiO}_2$  78.14,



$\text{SO}_3$  0.52,  $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  1.91,  $\text{CaO}$  8.88, and  $\text{Na}_2\text{O}$  10.55; in the transparent portion,  $\text{SiO}_2$  77.47,  $\text{SO}_3$  0.73,  $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  1.92,  $\text{CaO}$  9.66,  $\text{Na}_2\text{O}$  10.22. Now on eliminating from the numbers furnished by the devitrified portion, the ferric oxide, alumina, and sodium sulphate, a percentage composition can be calculated from the residue almost exactly corresponding with that calculated from a silicate of the constitution  $\text{Na}_2\text{Ca}(\text{SiO}_3)_2 + 6\text{SiO}_2$ .

To see whether any such silicate did exist, a portion of the glass was partially decomposed by treatment with hydrofluoric acid, and the residue was analysed. Its composition was found to be  $\text{SiO}_2$  95.02 per cent.,  $\text{Al}_2\text{O}_3$  0.70,  $\text{CaO}$  1.95,  $\text{Na}_2\text{O}$  2.33, instead of  $\text{SiO}_2$  80.3,  $\text{CaO}$  9.3,  $\text{Na}_2\text{O}$  10.4, as the above formula requires, and by further decomposition, in another experiment, a residue was obtained in which the percentage of  $\text{SiO}_2$  was 98.49. Hence the author concludes that silica, previously contained in solution in the glass, had crystallised out; he also shows that besides silica it is quite possible that certain definite silicates, richer in  $\text{SiO}_2$  than the surrounding glassy matrix, may crystallise out at the same time.

The author, in conclusion, states his conviction that glasses prone to devitrification do not consist of definite compounds, but are merely solutions of silica in glass (approximately  $\text{R}_2\text{O} \cdot 2\text{SiO}_2$  or  $\text{R}_2\text{SiO}_3 \cdot \text{SiO}_2$ ), which vary with the temperature in their power of holding in solution the dissolved substance, analogously with ordinary solutions. In apparently homogeneous glass we have a quickly solidified supersaturated solution, or an incomplete suppressed separation. But under favourable conditions, as for instance softening of the glass by heat, a change commences in the mass, and further separation of crystalline substance takes place. What applies here to the silica, applies also to other soluble compounds contained in the glass.

W. S.

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*Alterations in Potable Waters.* By J. MÜLLER (Arch. Pharm. [2], xlix, 27).

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## Organic Chemistry.

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### The Action of Potassium Sulphite on Bodies containing $\text{CCl}_3$ .

By B. RATHKE (Ann. Chem. Pharm., clxi, 149—171).

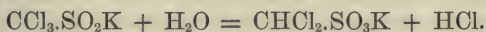
THE author having shown in a previous paper that all three atoms of the chlorine of trichloromethyl  $\text{CCl}_3$  are replaced by  $\text{SO}_3\text{K}$  when perchloromethylmercaptan is treated with potassium sulphite, while Strecker has shown that by treating chloroform with the same reagent only two atoms of the chlorine suffer this interchange, the third atom being replaced by hydrogen through the reducing action of the sulphite, it appeared desirable to submit some other bodies containing the group  $\text{CCl}_3$  to the same treatment.

*Trichloroformenesulphonic chloride*,  $\text{CCl}_3.\text{SO}_2\text{Cl}$ .—On treating this body with a solution of neutral potassium sulphite, the mixture becomes hot and large quantities of sulphurous acid escape. The following reaction takes place:—

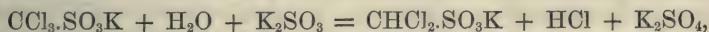


The result is therefore the same as if free sulphurous acid were employed.

The easily destroyed potassium salt of  $\text{CCl}_3.\text{SO}_3\text{H}$  formed on neutralization cannot be separated out, but the presence of the acid is placed beyond doubt, not only by its peculiar penetrating odour, but also by the immediate precipitation of trichloroformenesulphonic chloride on passing chlorine through the solution, a reaction characteristic of this acid and its salts. On boiling the solution of the potassium salt it is converted into potassium dichloroformenesulphonate (described by Kolbe)—



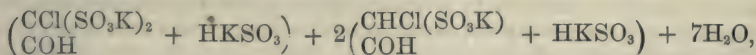
*Potassium trichloroformenesulphonate*,  $\text{CCl}_3.\text{SO}_3\text{K}$ , mixed in solution with potassium sulphite is first converted into  $\text{CHCl}_2.\text{SO}_3\text{K}$ , thus:—



and then at temperatures above  $100^\circ$  into potassium formenedisulphonate (methionate),  $\text{CH}_2(\text{SO}_3\text{K})_2$ , some potassium hyposulphate being also formed.

*Chloropicrin*,  $\text{CCl}_3.\text{NO}_3$ , digested at a general heat with a solution of the sulphite soon dissolves, the solution becoming acid. The salt,  $\text{CH}(\text{NO}_2)(\text{SO}_3\text{K})_2$ , is the product of the reaction. Potassium nitroformenedisulphonate, as this salt must be called, is easily dissolved by hot water and only with difficulty by cold. It crystallises in spheroidal groups of microscopic plates, bears a tolerably high temperature without change, but detonates rather smartly at a stronger heat; gives precipitates with baryta water and basic lead acetate; none with barium chloride, neutral lead acetate, silver nitrate, and mercurous nitrate.

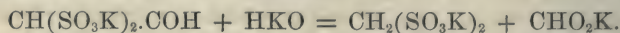
*Chloral hydrate*,  $\text{CCl}_3.\text{COH} + \text{H}_2\text{O}$ . Concentrated solutions of this body and the sulphite mixed in the cold yield chloroform, potassium formate, and the compound of chloral with acid potassium sulphite. But at a temperature approaching the boiling point the chlorine of the chloral is acted upon, and by adding the solution of the latter very gradually to the hot solution of the sulphite, loss of chloral by the production of chloroform can be avoided. On cooling and evaporating, a difficultly soluble salt,  $\text{CH}(\text{SO}_3\text{K})_2.\text{COH} + \text{HKSO}_3 + \text{H}_2\text{O}$ , and a very soluble salt—



besides a little  $\text{CH}_2(\text{SO}_3\text{K})_2$ , potassium formate, chloride, sulphate, and, what is worthy of remark, hyposulphate, are obtained.

The salt,  $\text{CH}(\text{SO}_3\text{K})_2.\text{COH} + \text{HKSO}_3 + \text{H}_2\text{O}$ , crystallises in indistinct rhombic plates, but when it is dissolved in hot water crystals containing

more water always separate out in the form of soft, brilliant white needles entangled together, and so minute that the whole appears amorphous. Cold supersaturated solutions can, however, be easily prepared, and on dropping a crystal of the original form into it, crystals of the same kind go on forming for a short time, though they are soon overgrown by the more hydrated crystals. This salt is the compound of acid potassium sulphite with chloral, in which two of the atoms of chlorine are replaced by  $\text{SO}_3\text{K}$  and the third by H. Boiled with potassium carbonate, it yields, besides the neutral sulphite, formenedisulphonate and formate, the behaviour of  $\text{CH}(\text{SO}_3\text{K})_2\cdot\text{COH}$  towards alkalis proving to be similar to that of chloral—



Lead peroxide gives the same salts together with lead sulphate.

On treating the cold solution of the salt with bromine until it remains permanently coloured, the sulphite is oxidized and the potassium aldehyde-disulphonate,  $\text{CH}(\text{SO}_3\text{K})_2\cdot\text{COH} + \text{H}_2\text{O}$ , set free. A similar destruction of the double salt is effected by boiling it for half an hour with hydrochloric acid. By boiling the new salt with acid sulphite, the double salt can readily be reproduced. Potassium aldehyde-disulphonate can be heated to  $130^\circ$  without undergoing change, and loses its water of crystallisation but slowly at  $170^\circ$ — $175^\circ$ ; above this it decomposes, swelling up into an exceedingly bulky twisted mass like "Pharaoh's serpents." The barium salt,  $\text{CH}(\text{SO}_3)_2\cdot\text{Ba}\cdot\text{COH} + 2\text{H}_2\text{O}$ , occurs in fine needles, is sparingly soluble in water, and can be recrystallised from hot acetic acid.

A solution of the potassium salt warmed with excess of bromine yields a much more soluble bromated salt,  $\text{CBr}(\text{SO}_2\text{K})_2\cdot\text{COH}$ , which crystallises out in needles on evaporating and cooling the solution. It is decomposed by heat, potassium bromide and sulphate mixed with a little carbon remaining as a residue. Neither silver nitrate, barium chloride, nor baryta-water precipitates its solutions. When it is boiled for a few seconds with potassium sulphite, the original double salt,  $\text{CH}(\text{SO}_3\text{K})_2\cdot\text{COH} + \text{H}\text{KSO}_3 + \text{H}_2\text{O}$ , separates out again on cooling. Boiled for half an hour with potassium carbonate and neutralized with acetic acid, the tolerably concentrated solution, after heating with alcohol and cooling, gives a deposit of microscopic plates or needles of another bromated salt. This salt, when boiled for a few seconds with potassium sulphite, yields on cooling crystals of  $\text{CH}_2(\text{SO}_3\text{K})_2$ ; it must therefore be  $\text{CHBr}(\text{SO}_3\text{K})_2$ , obtained, together with potassium formate, from  $\text{CBr}(\text{SO}_3\text{K})_2\cdot\text{COH}$  just as  $\text{CH}_2(\text{SO}_3\text{K})_2$  is obtained from  $\text{CH}(\text{SO}_3\text{K})_2\cdot\text{COH}$ .

The second salt obtained by the action of potassium sulphite upon chloral, which is readily soluble in water and has the complex formula already given, crystallises in large shining triclinic prisms, and can be obtained quite pure by repeated crystallisations from warm water. When heated, the salt swells up considerably, blackens, and leaves a residue of potassium sulphate and chloride and some carbon. Its water of crystallisation could not be directly determined, in consequence of decomposition taking place. It gives precipitates with silver and lead nitrates, soluble in nitric acid. Baryta-water precipitates barium sul-



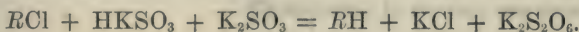
phite from its solutions, and was used to titrate the salt and thus check the results of analysis. After this precipitation there must be left in solution the salts  $\text{CCl}(\text{SO}_3\text{K})_2\cdot\text{COH}$  and  $\text{CHCl}(\text{SO}_3\text{K})\cdot\text{COH}$ , but all attempts to obtain them pure failed, only a syrupy liquid being formed on evaporation. This, however, on treatment with acid potassium sulphite, reproduced the crystalline double salt. Either component of this double salt would, by a further action of potassium sulphite, produce the salt,  $\text{CH}(\text{SO}_3\text{K})_2\cdot\text{COH} + \text{H}\text{KSO}_3$ , by the replacement of Cl in the one case by H and in the other by  $\text{SO}_3\text{H}$ ; so that the tendency to produce  $\text{CH}(\text{SO}_3\text{K})_2\cdot\text{COH}$  appears to be fulfilled in two distinct ways so far as regards the stages of the process.

It is remarkable that the two components of the double salt are produced in the proportion to form it, no excess of either being found in the mother-liquor. The circumstance therefore that the two only compounds intermediate between chloral and potassium aldehyde-disulphonate, which can result from the replacement of only two atoms of chlorine, can unite to form a double salt, actually occasions both of them to be produced and in a perfectly definite proportion.

During the digestion of chloral hydrate with potassium sulphite, a strong penetrating smell is given off quite distinct from that of either chloroform or chloral, some of the chloral being apparently converted into mono- and dichloraldehyde. A very large quantity of it appears to be changed into these or other volatile bodies, but the investigation has not been pursued in this direction.

*Trichloroacetic Acid*,  $\text{CCl}_3\cdot\text{CO}_2\text{H}$ .—On gradually adding to a nearly boiling solution of the sulphite a solution of trichloroacetic acid, sulphurous acid first escapes and then carbonic acid and chloroform. The solution boiled till it ceases to smell of chloroform contains, besides sulphate and a not inconsiderable quantity of hyposulphate, a very soluble salt which crystallises in beautiful perfect square octohedrons with the basal pinacoids predominating, like the crystals of potassium ferrocyanide. They undergo no change in a vacuum over sulphuric acid, but lose water at  $100^\circ$ . The salt begins to decompose above  $165^\circ$ , and when heated sufficiently, swells up, burns with a sulphur-flame, and leaves a residue of potassium chloride and sulphate discoloured by carbon. It has the formula  $\text{CHCl}(\text{SO}_3\text{K})\cdot\text{CO}_2\text{K} + \frac{1}{2}\text{H}_2\text{O}$ . Its solution is not precipitated by baryta-water, neutral or basic lead acetate, or silver nitrate. From the behaviour of the corresponding salts obtained from chloral, it might be expected that this salt would behave like trichloroacetic acid when treated with alkalis, but after being boiled for an hour with concentrated potash it remains unchanged. On the other hand, its aqueous solution kept for some hours at  $140^\circ$  is partly decomposed, with liberation of sulphurous acid. Kept at this temperature for some hours with potassium sulphite, it yields a considerable quantity of potassium chloride, so that probably the Cl becomes replaced by H or by  $\text{SO}_2\text{K}$ , but a pure product could not be obtained.

The hyposulphate produced in the action of the sulphite upon the above chlorides must result from a molecule of  $\text{H}\text{KSO}_3$  and one of  $\text{K}_2\text{SO}_3$  giving up H and K respectively, and the residues then uniting, thus:—



The formation of hyposulphate by the gradual withdrawal of hydrogen from the acid sulphite can easily be directly shown by digesting a hot solution of this salt for some time with lead peroxide, when potassium hyposulphate crystallises out on cooling.

E. D.

**Some Cases of the Formation of Chemical Compounds by Insufficient Affinities.** By B. RATHKE (*Ann. Chem. Pharm.*, clxi, 171—174).

A REACTION which by itself cannot take place, because it would involve a fixation of heat, may do so in conjunction with either another reaction or a change of physical condition, when the total result is a liberation of heat.

Thus (see preceding paper)  $\text{CCl}(\text{SO}_3\text{K})_2\cdot\text{COH} + \text{HKSO}_3$  and  $\text{CHCl}(\text{SO}_3\text{K})\cdot\text{COH} + \text{HKSO}_3$  are neither of them formed alone, because their formation would fix heat; but the two together form in a fixed proportion and unite with each other and with water of crystallisation, because the operations altogether cause a liberation of heat. So with other cases of *predisposing affinity*, the influence of which, in some cases, we must still recognise.

Another case is that of the action of iodine upon hydrogen sulphide, which has been investigated by Naumann (*Ann. Chem. Pharm.*, cli, 145).

Again, from a mixed solution of potassium thiosulphate and acid sulphite, potassium trithionate crystallises out, although in the supernatant liquid this salt cannot be detected. Here, if the salt were to form in solution there would be a fixation of heat, whereas by forming in the solid state, its production is attended with liberation of heat.

E. D.

**Abietene, a New Hydrocarbon.** By WILLIAM WENZELL (*Pharm. Journ. Trans.* [3], ii, 789).

THIS hydrocarbon is the product of the distillation of the exudation of a coniferous tree (*Pinus sabiniana*, or nut-pine), indigenous in California; the resin exudes from incisions which are made in the tree during winter. The hydrocarbon was found to distil almost constantly about  $101^\circ$ ; its specific gravity is  $\cdot 694$  at  $16\cdot 5^\circ$ ; it is nearly insoluble in water, and soluble in 5 parts of alcohol containing 95 per cent.

Hydrochloric acid gas and sulphuric acid do not act on it; nitric acid on boiling attacks it moderately; chlorine gives rises to substitution-products. It burns with a brilliant, white, smokeless flame, and dissolves fixed and volatile oils, except castor-oil, which is insoluble in it. Its vapour has powerful anæsthetic properties; it has a penetrating odour, resembling oil of oranges. No analysis of this hydrocarbon, or of its compounds, is given, but the distinguishing properties between it and terebene are noticed at some length.

A. P.

**Hydrobromides and Hydrochlorides of Allylene.** By

M. REBOUL (Compt. rend., lxxiv, 669—672).

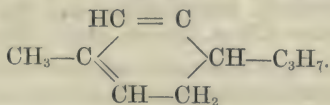
ALLYLENE unites directly and rapidly in the cold, with a concentrated aqueous solution of hydrobromic acid employed in great excess. With an acid marking  $66^{\circ}$  Baumé, and at  $0^{\circ}$ , the process is complete in five or six hours. The oily body obtained is dihydrobromide of allylene,  $C_3H_4.H_2Br_2$ , with a small quantity of the monohydrobromide. On rectification, a liquid is obtained, having a density of 1.875 at  $10^{\circ}$ , and boiling at  $114^{\circ}$ — $115^{\circ}$ . This body is isomeric with propylene bromide,  $C_3H_6.Br_2$ , but has a much less fragrant odour, and appears to be identical with Linnemann's *methylbromacetol*. The dihydrobromide, submitted to the action of alcoholic potash, loses one molecule of hydrobromic acid, and is reduced to the state of monohydrobromide,  $C_3H_4.HBr$ , the density of which is 1.39 at  $9^{\circ}$ , and the boiling point  $48^{\circ}$ — $49^{\circ}$ . Allylene hydrobromide, although isomeric with bromopropylene, is quite a distinct body. The former has a lower boiling point, and is much more readily acted upon by a concentrated solution of hydrobromic acid.

Allylene also unites directly in the cold, with concentrated hydrochloric acid, but much less rapidly than with hydrobromic acid. The oily product is a mixture of mono- and di-hydrochloride of allylene, in which the latter largely predominates. On rectification the dihydrochloride is found to boil at  $69^{\circ}$ — $70^{\circ}$ , and is probably identical with Friedel's *methylchloracetol*.

J. B

**Cymene from Oil of Turpentine.** By A. OPPENHEIM (Deut. Chem. Ges. Ber., v, 94—100).

WHEN finely powdered terpin,  $C_{10}H_{18}(OH_2)$ , is mixed with bromine, and the mixture heated to  $50^{\circ}$ , or allowed to stand at the common temperature, the dibromide  $C_{10}H_{16}Br_2$  is formed, a colourless, heavy oil, which decomposes when heated, with loss of hydrobromic acid. The same dibromide is obtained by adding bromine to oil of turpentine or oil of lemons at a low temperature. When this compound is heated with aniline, it loses two molecules of hydrobromic acid, and the hydrocarbon  $C_{10}H_{14}$  is formed, which boils at  $175.5^{\circ}$ — $178.5^{\circ}$ , and appears to be identical with  $\alpha$ -cymene or methyl-propyl-benzene from cuminal oil. This is the more probable as both cymene and oil of turpentine occur as essential oils, and yield on oxidation terephthalic acid. Oil of turpentine is therefore cymene hydride, and belongs to the additive compounds of the aromatic group. Baeyer has pointed out that in these additive compounds the partial separation of the carbon-atoms of the benzene-ring most readily takes place where alcohol-radicals have entered. The constitution of oil of turpentine is therefore probably the following:—



C. S.



### Chlorine Substitution-products of Ethyl Chloride. By W. STAEDL (Zeitschr. f. Chem. [2], viii, 513).

IN continuation of his former paper on this subject (*Chem. Soc. J.*, 1871, 696) the author concludes that ethylene chloride is not formed by the action of chlorine on ethyl chloride. The isomeric ethylidene chloride thus produced boils at 59° (after purification from traces of ethyl chloride by agitation with mercury, which decomposes this substance), and is identical with the body obtained by the action of phosphorus pentachloride on aldehyde, and with the chlorinated ethyl chloride obtained as a bye product in the manufacture of chloral.

By the action of chlorine (not dried) on *pure* dichlorinated ethyl chloride of boiling point 74°, there were formed (A) a body of formula  $C_2H_2Cl_4$ , boiling at 127·5°; (B) a body of formula,  $C_2HCl_5$ , boiling at 157°—159°; (C) carbon trichloride,  $C_2Cl_6$ , of melting point 181°. Regnault obtained a body of formula,  $C_2H_2Cl_4$ , from chlorine and ethyl chloride, boiling at 102°. Neither Geuther (*Zeitschr. f. Chem.* [2], vii, 147,) nor Welters (*Journ. f. pr. Chem.* [2], iv, 57,) could obtain this substance, although the former chemist obtained a body of this composition, boiling at 133°—136°, from chlorine and impure monochlorinated ethyl chloride, and also from impure dichlorinated ethyl chloride.

The author gives the following table:—

Monochlorinated ethyl chloride,		
Ethyl chloride: 11°·5.	or ethylidene chloride: 59°.	Ethylene chloride: 84°.
$\begin{array}{c} CH_2Cl \\   \\ CH_3 \end{array}$	$\begin{array}{c} CHCl_2 \\   \\ CH_3 \end{array}$	$\begin{array}{c} CH_2Cl \\   \\ CH_2Cl \end{array}$
Dichlorinated ethyl chloride: 74°.		Monochlorinated ethylene chloride: 115°.
$\begin{array}{c} CCl_3 \\   \\ CH_3 \end{array}$		$\begin{array}{c} CHCl_2 \\   \\ CH_2Cl \end{array}$
Trichlorinated ethyl chloride: 127·5°.		Dichlorinated ethylene chloride, 147°.*
$\begin{array}{c} CCl_3 \\   \\ CH_2Cl \end{array}$		$\begin{array}{c} CHCl_2 \\   \\ CHCl_2 \end{array}$
Tetrachlorinated ethyl chloride, or trichlorinated ethylene chloride: 158°.		Carbon sesquichloride, melting point, 181°.
$\begin{array}{c} CCl_3 \\   \\ CHCl_2 \end{array}$		$\begin{array}{c} CCl_3 \\   \\ CCl_3 \end{array}$

C. R. A. W.

### Synthesis of Normal Butyl Alcohol. By E. LINNEMANN (Ann. Chem. Pharm. clxi, 178).

BUTYRIC acid free from higher homologues, and containing but traces of acetic acid, was converted into butyryl chloride by phosphorous chloride.

\* Paternò and Pisati, *Nuovo Cimento* [2], iv, 401.

The yield of pure chloride, boiling at  $100^{\circ}$ — $101.5^{\circ}$ , varied from 41 to 96 grams from 100 of acid, 120 being theoretically obtainable. The chloride was then converted into anhydride by heating, first in the water-bath, and then at higher temperatures, with the pure acid, the yield being from 70 to 110 grams of anhydride from 100 of chloride, 149 being theoretically obtainable. The direct action of phosphorus or phosphoric chloride on butyric acid gives a very small yield, and that of butyryl chloride on calcium butyrate does not give a good result, unless the lime salt be previously dried at  $150^{\circ}$  in a stream of dry air. The pure anhydride boils at  $191^{\circ}$ — $193^{\circ}$ .

Five per cent. sodium amalgam, as little oxidised as possible, and in lumps the size of peas, was moistened with butyric acid, and added cautiously to the anhydride, not more than 20 grams of the latter being employed at a time, with 200 grams of the amalgam, and the vessel being cooled by ice-water; finally ice was added, then water, and the oily layer was removed and saponified with potash. The yield was better when the anhydride was previously diluted with the acid, and was higher still when a mixture of acid and chloride was used. After repeated boiling with caustic potash solution to decompose butyl butyrate, the alcohol was dehydrated by solid potash, and finally by heating in a sealed tube to  $110^{\circ}$ — $120^{\circ}$ , with powdered caustic baryta.

By distilling a mixture of 1 equiv. calcium butyrate and 2 equivs. calcium formate, butyric aldehyde was obtained, which was converted into alcohol in the same way as that employed for propionic aldehyde; the crude alcohol thus obtained contained isobutyl alcohol, trimethyl carbinol, and methylic alcohol, as by treatment with gaseous hydriodic acid and fractional distillation of the product, the iodides of methyl, trimethyl-carbinyl, isobutyl, and normal butyl were obtained, boiling respectively at  $41^{\circ}$ — $46^{\circ}$ ,  $97^{\circ}$ — $99^{\circ}$ ,  $115^{\circ}$ — $125^{\circ}$ , and  $127.9^{\circ}$ — $129.1^{\circ}$ . After repeated rectification, the latter substance had the corrected boiling point  $129.95^{\circ}$ , and the sp. gr. 1.5909 at  $16^{\circ}$ .

The following table shows the comparative yields of alcohol obtained from 100 grams butyric acid by the above methods:—

60 grams anhydride.*		22 grams aldehyde.	96 grams chloride.
Reduced <i>per se</i> .	Diluted with butyric acid.		
1.2 grams alcohol ( $100^{\circ}$ — $125^{\circ}$ ).	4.8 grams alcohol ( $100^{\circ}$ — $125^{\circ}$ ).	12.3 grams alcohol ( $80^{\circ}$ — $120^{\circ}$ ).	13.4 grams alcohol ( $100^{\circ}$ — $125^{\circ}$ ).

The alcohol obtained from the anhydride boiled at  $114^{\circ}$ — $116^{\circ}$ ; thickened at  $-17^{\circ}$ ; was optically inactive; had the sp. gr. 0.8112 at  $15^{\circ}$ ; and furnished an iodide, boiling at  $125^{\circ}$ — $129^{\circ}$ ; oxidation by potassium dichromate gave normal butyric acid, recognised by the properties and analysis of the calcium and silver salts.

C. R. A. W.

\* 57 grams acid gave 55 of chloride; this, and 42 of acid, gave 60 of anhydride.

**Pure Normal Butyl Derivatives.** By E. LINNEMANN (*Ann. Ch. Pharm.*, clxi, 190).

PURE *normal butyl alcohol* was obtained by converting into iodide the crude alcohol obtained by reducing butyric aldehyde, chloride, or anhydride, collecting the portion boiling at  $127^{\circ}$ — $130^{\circ}$ , converting this into benzoate, purification by fractional distillation, and, finally, saponification with potash, and dehydration with caustic baryta in a sealed tube at  $110^{\circ}$ — $120^{\circ}$ . Another specimen was similarly obtained from a mixture of pure acetate, propionate and butyrate. These two specimens had respectively the corrected boiling-points  $116.88^{\circ}$  and  $116.96^{\circ}$ . The alcohol from the benzoate was optically inactive, did not solidify at  $-22^{\circ}$ , had the specific gravity 0.8135 at  $22^{\circ}$ , was soluble in 12 volumes of water at  $22^{\circ}$ , and dissolved 0.15 volumes of water at  $22^{\circ}$ . With gaseous hydriodic acid, it gave an iodide of which the corrected boiling-point was  $129.65^{\circ}$ , and the sp. gr. 1.5804 at  $18^{\circ}$ . As the iodide from butyric anhydride was found to boil at  $129.97^{\circ}$ , and that from butyric aldehyde at  $129.95^{\circ}$ , the mean boiling-point  $129.82^{\circ}$  may be taken as correct.

By treating this pure iodide with pure silver benzoate, acetate, propionate, and butyrate, the corresponding butyl ethers were prepared; also butyl chloride from the iodide and mercury chloride, and butyl bromide from the pure alcohol and hydrobromic acid. The physical properties of these products were as follows:—

	Benzoate.	Acetate.	Propionate.	Butyrate.	Chloride.	Bromide.
Corrected boiling point	247.32	124.36	145.99	164.77	77.96	$\left\{ \begin{array}{l} 99.94 \\ 99.83 \end{array} \right.$
Specific gravity .....	1.0000 at $20^{\circ}$	0.8768 at $23^{\circ}$	0.8828 at $15^{\circ}$	0.8760 at $12^{\circ}$	0.8972	1.2990 at $20^{\circ}$
Solubility in water .....	Insoluble. }	1n 90 parts } at $20^{\circ}$ }	—	Insoluble.	Insoluble.	—

The bromide from the alcohol boiled at  $99.94^{\circ}$ , while another specimen from the iodide and copper bromide boiled at  $99.83^{\circ}$  (corrected): hence  $99.88^{\circ}$  may be taken as the true mean boiling-point.

*Brominated normal butyl bromide* was obtained by heating 8 parts of the normal bromide and 9 of bromine for five hours at  $150^{\circ}$ ; it boiled at  $166^{\circ}$ — $167^{\circ}$ ; hence the author concludes that it is identical with Wurtz's dibromide of ethyl-vinyl (*Ann. Chem. Pharm.*, clii, 21), boiling at  $166^{\circ}$ , and only isomeric with the dibromide of methyl-allyl, boiling at  $156^{\circ}$ — $159^{\circ}$  (*Ann. Chem. Pharm.*, cl, 109), from both of which, again, the dibromide of isobutylene differs, its boiling-point being  $149^{\circ}$ . He gives the following formulæ:—

$\alpha$ -butylene = ethyl vinyl	$\beta$ -butylene = methyl allyl.	$\gamma$ -butylene. Butylene from isobutyl
= butylene from normal butyl alcohol.	Butylene from ethyl methyl carbinol.	alcohol, or from trimethyl carbinol.
CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>
CH <sub>2</sub>	CH	CH.CH <sub>3</sub>
CH	CH	CH <sub>2</sub>
CH <sub>2</sub>	CH <sub>3</sub>	
Dibromide boils at 166°—167°.	Dibromide boils at 156°—159°.	Dibromide boils at 149°.



*Note by the Abstractor.*—The author regards allyl iodide as  $\begin{matrix} \text{CH}_3 \\ \text{CH} \\ \text{CHI} \end{matrix}$ , and

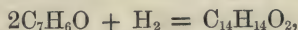
not as  $\begin{matrix} \text{CH}_2\text{I} \\ \text{CH} \\ \text{CH}_2 \end{matrix}$ ; this latter formula would represent methyl-allyl as identical with ethyl-vinyl. Chapman (*Chem. Soc. J.* [2], v, 28) finds that the main portion of the dibromide of ethyl-vinyl from vinyl bromide and zinc ethyl boils at  $158^\circ$ — $160^\circ$ . The author does not appear to admit of the possible existence of a fourth butylene, viz., methylated trimethylene,  $\text{CH}_2 \begin{matrix} \text{CH}.\text{CH}_3 \\ | \\ \text{CH}_2 \end{matrix}$ .

C. R. A. W.

### Butylene Glycol, a new Condensation-product of Aldehyde.

By AUG. KEKULÉ (*Deut. Chem. Ges. Ber.*, v, 56).

THE author has succeeded in realising in the fatty series the reaction analogous to that by which benzaldehyde is converted, by assumption of hydrogen, and simultaneous condensation, into hydrobenzoin:—



having obtained butylene glycol from acetaldehyde—



Sodium amalgam was added to an acidulated dilute aqueous solution of aldehyde; the liquid separated from the mercury was filtered, neutralised, and distilled in order to separate the alcohol formed; other bye-products, not yet examined, were afterwards removed by shaking with ether; the aqueous liquid was then evaporated almost to dryness, mixed with alcohol, filtered off from sodium chloride, and distilled. The butylene glycol was finally obtained from the portion of higher boiling point by repeated fractional distillation. Even under the most favourable conditions, however, the yield is extremely small.

Butylene glycol thus prepared boils at  $203.5^\circ$ — $204^\circ$ . It is a clear, syrupy liquid, of sweet, but slightly pungent taste; easily soluble in water and alcohol, insoluble in ether.

The results of various oxidation experiments with the new body were as follows:—With nitric acid the products were acetic and oxalic acid, and some carbonic anhydride; on oxidation with aqueous chromic acid carbonic anhydride and much acetic acid were obtained, but no oxalic acid, which is further oxidised by the reagent. In both cases the presence of crotonic aldehyde was rendered evident by its characteristic odour, and small quantities of ordinary aldehyde were also detected with certainty.

These results the author considers lead conclusively to the formula  $\text{CH}_3.\text{CH}(\text{OH}).\text{CH}_2.\text{CH}_2(\text{OH})$ . The appearance of crotonic aldehyde renders it probable that the first reaction consists in the separation of

water and formation of crotonic alcohol,  $\text{CH}_3\text{—CH=CH—CH}_2\text{OH}$ , which is then oxidised to crotonic aldehyde. In confirmation of this view, it was found that the latter yields exactly the same oxidation-products as butylene-glycol. In conclusion, the author points out the different action of acid oxidising agents and of potassium hydrate, which latter is not a true oxidising agent, inasmuch as it also gives up hydrogen.

H. E. A.

**On Monoallylin and Glycerin-Ether.** By B. TOLLENS (Deut. Chem. Ges. Ber., v, 68—72).

THE author calls attention to the difference between the monoallylin obtained by him as a bye-product in the preparation of allyl alcohol, and the glycerin-ether supposed by Gegerfelt, Linnemann, and Zotta to be identical with it (*Journ. Chem. Soc.* [2], x, 61, 134).

He has prepared afresh a quantity of monoallylin from the syrup remaining as residue from the rectification of crude allyl alcohol. (In this residue he also obtained glycerin-ether in the product passing over at  $169^\circ\text{—}172^\circ$ , having, according to analysis, the composition  $\text{C}_6\text{H}_{10}\text{O}_3$ . The monoallylin boiled at  $225^\circ\text{—}240^\circ$ , and had, according to analysis, the composition  $\text{C}_6\text{H}_{12}\text{O}_3$ , thus differing essentially from glycerin-ether. Monoallylin (unlike glycerin ether) is partly decomposed by distillation, with formation of allyl alcohol.

The action of bromine on monoallylin distinguishes it readily from glycerin-ether. Bromine dropped into an aqueous solution of monoallylin is decolorised, and an oil (monoallylin dibromide) separates. No apparent reaction is caused by adding bromine to a solution of glycerin-ether. Both Gegerfelt and the author were unable to find monoallylin in the liquid obtained by the dry distillation of the residue left on distilling glycerin with oxalic acid.

Linnemann and v. Zotta have asserted that in their preparation of glycerin ether they discovered a new simple transition from the fatty to the aromatic series. The author has examined the product formed in the preparation of allyl alcohol, which boiled at about  $180^\circ$ , and found considerable traces of phenol in it (by Landolt's method). No appreciable quantity of phenol could be found in the products which boiled at a higher temperature, nor in the resin formed by heating glycerin ether with potash; but by heating the acrolein resin (obtained as a bye-product) with potash, a body was formed which smelt like resorcin, was very soluble in water and ether, and gave a violet-red colour when mixed with ferric chloride.

The author calls attention to the inference which Linnemann draws from his observations on the decomposition of the nitrites of amines (*Journ. Chem. Soc.* [2], x, 133), viz., that the question whether allyl alcohol contains the group  $\text{CH}_3$  may be decided by the decomposition of allylamine nitrite.

The author considers that the non-hydrogenising of allyl alcohol, the non-formation of acetic acid by oxidation of the same, and the formation of dibromopropionic acid by oxidation of the bromide of allyl alcohol, respectively indicate that in allyl alcohol the carbon-atoms are doubly combined, that the group  $\text{CH}_3$  does not exist in it, and that it

contains the group  $\text{CH}_2\text{OH}$  ; and he does not believe that the suggested reaction could satisfactorily settle the question which has been raised.

C. C.

### Isomerides of Trichlorhydrin, and Reproduction of Glycerin.

By C. FRIEDEL and R. D. SILVA (Compt. rend., lxxiv, 805—809).

By the action of chlorine, aided by sunlight, upon methyl-chloracetol the authors have obtained a single trichloride,  $\begin{Bmatrix} \text{CH}_3 \\ \text{CCl}_2 \\ \text{CH}_2\text{Cl} \end{Bmatrix}$ , which boils at  $123^\circ$ .

The same compound is formed by the action of chloride of iodine on methyl-chloracetol, and by fixation of chlorine upon chloropropylene. This body, by treatment with water, gave a soluble non-volatile substance, the composition of which is not yet definitely settled, together with small quantities of two bodies, both having the formula  $\text{C}_3\text{H}_4\text{Cl}_2$ . The one boils between  $79^\circ$  and  $85^\circ$ , and the other between  $91^\circ$  and  $97^\circ$ . The authors have succeeded in isolating both these bodies from the product of the action of chlorine on chloro-propylene.

From propylene dichloride, on the other hand, by heating in sealed tubes with dry iodine chloride, an oily liquid was obtained, and this submitted to distillation gave three principal products. The first was unchanged propylene dichloride. The second, boiling at about  $140^\circ$ ,

was the compound  $\begin{Bmatrix} \text{CH}_3 \\ \text{CHCl} \\ \text{CHCl}_2 \end{Bmatrix}$ , which is also formed by the action of chlorine upon propylene chloride in sunlight.

The third, boiling at about  $155^\circ$ , was trichlorhydrin, mixed with a trace of a tetrachloride, which could not be completely separated. Its identity was established by its physical properties, and by the fact that it furnished glycerin when heated with water to  $170^\circ$ . The glycerin thus generated was satisfactorily recognisable by its physical as well as by its chemical characteristics.

The propylene dichloride used in these experiments was prepared by the aid of allyl iodide, but care was taken to avoid the presence of any allylic compound.

The authors therefore claim to have produced glycerin from a body, namely, propylene dichloride, which may be prepared without employing glycerin itself as the starting point.

W. A. T.

### A new class of compounds of Dulcite with Hydracids. By G. BOUCHARDAT (Compt. rend., lxxiv, 866—868).

DULCITE is found to dissolve easily in aqueous hydrochloric acid (saturated at zero), with slight decrease of temperature. After standing twenty-four hours at a low temperature, voluminous crystals of the hydrochloride of dulcite are deposited. They have the composition  $\text{C}_6\text{H}_{14}\text{O}_4 \cdot \text{HCl} + 3\text{H}_2\text{O}$ . This compound is very unstable, and can exist

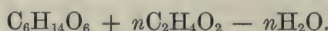


only in an atmosphere saturated with hydrochloric acid. The whole of the hydrochloric acid is given off when the crystals are exposed to a current of air. The corresponding compounds of dulcite with hydrobromic and hydriodic acids have been obtained, the two latter being somewhat more stable than the hydrochloride.

A. P.

**Acetic Ethers from Dulcite.** By G. BOUCHARDAT (Compt. rend., lxxiv, 665—668).

DULCITE submitted to the action of acetic acid produces a great number of neutral compounds, some of which belong to the series of ethers of dulcite having the general formula—



and others to the series of ethers of dulcitan, having the general formula—



*Diaceto-dulcite*,  $\text{C}_{10}\text{H}_{18}\text{O}_6$ . Crystalline scales, fusible at  $176^\circ$ , volatile without residue on ignition; inodorous, insipid, slightly soluble in cold water, alcohol, or ether, soluble in lukewarm water; saponified by dilute alkalis.

*Diaceto-dulcitan*,  $\text{C}_{10}\text{H}_{16}\text{O}_7$ . Volatile without residue on ignition; tastes very bitter; soluble in water, alcohol, and ether. At the ordinary temperature this substance is a colourless liquid, of the consistence of oil beginning to congeal.

*Hexaceto-dulcite*,  $\text{C}_{18}\text{H}_{26}\text{O}_{12}$ . Hard, friable, crystalline plates, fusible at  $171^\circ$ ; sublimes at  $200^\circ$ — $220^\circ$  without alteration of its chemical composition. The sublimed product acquires for a time different properties, but gradually resumes its former state.

*Tetraceto-dulcitan*,  $\text{C}_{14}\text{H}_{20}\text{O}_9$ . Colourless and resinous in appearance; sublimes without residue; insupportably bitter; has a disagreeable odour when warm; nearly insoluble in water, soluble in alcohol and ether, and saponified by alkali.

*Pentacetomono-chlorhydro-dulcite*,  $\text{C}_{16}\text{H}_{23}\text{ClO}_{10}$ , obtained by acting on dulcite with a mixture of acetic and hydrochloric acids, is an unstable compound, which, when heated in water, decomposes into pentaceto-dulcite and hydrochloric acid.

*Pentaceto-dulcite*,  $\text{C}_{16}\text{H}_{24}\text{O}_{11}$ . Crystalline body with properties very similar to those of hexaceto-dulcite, but less soluble in alcohol and ether. Heated for a long time to about  $200^\circ$ , it is partially transformed into pentaceto-dulcitan, with separation of water.

J. B.

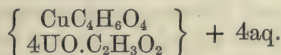
**Pyruvin.** By M. SCHLAGDENHAUFFEN (Compt. rend., lxxiv, 672).

WHEN glycerin is heated in a retort with tartaric acid, crystals of pyruvin are formed in the neck of the receiver. This body sublimes at the temperature of the water-bath in brilliant scales, fusible at  $78^\circ$ , soluble in alcohol, ether, carbon disulphide, benzene, and especially in

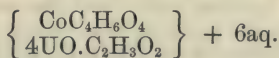
chloroform. Water dissolves and decomposes it, and the solution, at first neutral, soon becomes acid. Pyruvin boils at  $242^{\circ}$ , changes colour during ebullition, and becomes acid. J. B.

**Double Salts of Uranium Acetate.** By C. RAMMELSBERG (Pogg. Ann. cxlv, 158—162).

1. *Uranium-copper Acetate*.—Precipitated as green crystals from a mixture of solutions of the two salts. Crystal-system—hexagonal rhombohedral. The formula given is—



2. *Uranium-cobalt Acetate*.—Small yellow-brown crystals, belonging to the dimetric system, having the formula—

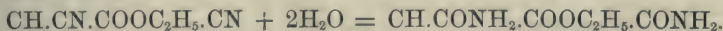


This salt, heated to  $130^{\circ}$ , loses all the six equivalents of water, and becomes violet-coloured.

M. M. P. M.

**Action of Potassium Cyanide on Dichloroacetic Acid.** By D. AMATO (Gazzetta Chimica Italiana, 690—695).

As Kolbe (*Ann. Ch. Pharm.*, cxliii) and Hugo Müller (*Jour. Chem. Soc.*, 1864, p. 109) obtained malonic acid by the successive action of potassium cyanide and hydrate on monochloroacetic acid, the author was desirous of ascertaining if more than two carboxyls,  $\text{COOH}$ , could unite with the same atom of carbon, and for this purpose determined to study the action of potassium cyanide on dichloroacetic acid. Ethyl dichloroacetate was digested, at a temperature below  $100^{\circ}$ , with a solution of potassium cyanide in dilute alcohol until the odour of hydrocyanic acid had disappeared. After filtration from the potassium chloride formed, and separation of the alcohol, the liquid was agitated with ether, and the ethereal solution evaporated; it then left a dense liquid, which on standing, solidified to a crystalline mass. The aqueous solution separated from the ether was found to contain oxalic, malonic, and glycolic acids. The residue left on evaporating the ethereal solution was purified by crystallisation from alcohol and water. It is scentless and tasteless; melts at  $190^{\circ}$ — $191^{\circ}$ ; has a neutral reaction; is very soluble in ether, and moderately so in alcohol. It is readily soluble in hot water, and but slightly in cold water, crystallising from the solution in small prisms; its aqueous solution is decomposed by potassium hydrate in the cold, with evolution of ammonia. The author assigns to the crystals the composition  $\text{CH.CONH}_2\text{COOC}_2\text{H}_5\text{CONH}_2$ , and believes that the ethylic dicyanacetate at first formed is converted by the action of water, in the presence of excess of acetic acid, into the amidated ether of a new acid.



Ethyl dicyanacetate.

New compound.

This compound, by the action of potassium hydrate, should yield a salt of the corresponding acid,  $\text{CH}_3(\text{COOH})_3$ ; but the author on making the experiment, only obtained the products of its decomposition, namely, oxalic, malonic, and glycolic acids.

C. E. G.

**Dibromopropionic Acid.** By G. MÜNDE and B. TOLLENS (Deut. Chem. Ges. Ber., v, 68).

THE authors have formed dibromopropionic acid ( $\text{C}_3\text{H}_4\text{Br}_2\text{O}_2$ ) by oxidation of allyl-alcohol bromide, also some salts and ethers of the acid. This dibromopropionic acid melts at  $64^\circ$ — $64.5^\circ$ , and boils at  $220^\circ$ — $240^\circ$ . The dibromopropionic acid prepared by Friedel from propionic acid melts at  $65^\circ$ — $70^\circ$ .

From this fact the authors infer that the two acids are identical, that allyl-alcohol bromide contains the group  $\text{CH}_2\text{OH}$ , and may be represented by the formula  $\text{CH}_2\text{Br}.\text{CHBr}.\text{CH}_2\text{OH}$ .

Some difficulty was experienced in preparing salts of the acid, owing to the formation of metallic bromides.

Those obtained were the silver, lead, and potassium salts, which may be represented by the general formula  $\text{C}_3\text{H}_3\text{BrMO}_3$ . The action of ammonia on the acid produced ammonium-amido bromopropionate ( $\text{C}_3\text{H}_3\text{Br}.\text{NH}_2(\text{NH}_4)\text{O}_2$ ).

The ethyl, methyl, and allyl ethers were easily obtained by passing hydrogen chloride into a solution of the acid in the respective alcohols—

Methyl ether. . . . .	$\text{C}_3\text{H}_3\text{Br}_2(\text{CH}_3)\text{O}_2$ : B.P. $203^\circ$ .
Ethyl ether . . . . .	$\text{C}_3\text{H}_3\text{Br}_2(\text{C}_2\text{H}_5)\text{O}_2$ : B.P. $211^\circ$ — $214^\circ$ .
Allyl ether . . . . .	$\text{C}_3\text{H}_3\text{Br}_2(\text{C}_3\text{H}_5)\text{O}_2$ : B.P. $215^\circ$ — $220^\circ$ .

C. C.

**Synthesis of Normal Butyric Acid.** By E. LINNEMANN and V. v. ZOTTA (Ann. Chem. Pharm., clxi, 175).

PURE fermentation propylic alcohol was converted into propyl iodide, and this into cyanide by heating for 30 hours with alcoholic potassium cyanide. By the action of caustic potash on this cyanide, normal potassium butyrate was obtained, from which the acid was obtained by neutralisation with dilute hydrochloric acid, evaporation to dryness, treatment with dry hydrochloric acid gas, and finally distillation over phosphoric anhydride. The corrected boiling point of the pure acid was  $162^\circ$ — $163^\circ$ , and its sp. gr. at  $14^\circ$ , 0.9601, the butyric acid of fermentation boiling at  $162.32^\circ$ , and having the sp. gr. 0.9580 at  $14^\circ$ ; the pure acid readily solidified in a mixture of salt and snow, and was optically inactive. The silver salt was anhydrous, and dissolved in 200 parts of water at  $14^\circ$ , while that from the fermentation acid dissolved in 202 parts at  $14^\circ$ . The calcium salt contained (after drying at  $100^\circ$ )  $\text{C}_4\text{H}_7\text{CaO}_2 + \text{H}_2\text{O}(\text{Ca} = 20)$ , and was less soluble in hot than in cold



water; 1 part of the salt from the synthesised acid dissolved in 3·2 parts of water at 15°, while that from the fermentation acid required 3·5 at 14°. The barium salt dried at 100° was anhydrous; 1 part of the artificial acid required 2·48 of water for its solution at 14°, while 1 part of the fermentation product required 2·43 at 14°. The ethylic ether had the corrected boiling-point 121·05°, and the sp. gr. 0·8953 at 18°, while that from pure ethyl iodide and fermentation silver butyrate had the corrected boiling-point 121·07°, and the sp. gr. 0·9003 at 18°.

Hence the authors consider that the identity of the acids from fermentation and from propylic cyanide is demonstrated.

C. R. A. W.

**Formation of Salicylic Acid from the Bromo-benzoic Acid melting at 155°.** By H. HUEBNER (*Zeitsch. f. Chem.* [2], viii, 562—566.

SEVERAL chemists have observed that on fusing this bromo-benzoic acid with caustic potash, there is always some *salicylic acid* formed besides oxybenzoic acid. This formation of salicylic acid is caused, not by any molecular change, or by impurities contained in the bromo-benzoic acid, but by a secondary reaction, viz., by the combination of potassium carbonate with phenol, of which a small quantity is always formed. This is proved by the fact that when pure phenol is fused with a large excess of potash and some sodium carbonate, a small quantity of salicylic acid is obtained.

C. S.

**Methylmercaptantrisulphonic Acid, Methylmercaptandisulphonic Acid, and Methylalcoholtrisulphonic Acid.** By MAX ALBRECHT (*Ann. Chem. Pharm.*, clxi, 129—148).

THE author has investigated some of the reactions of perchlormethylmercaptan,  $\text{CSCl}_4$ .

1.  $\text{CSCl}_4$  is added slowly to a concentrated solution of neutral potassium sulphite, when a new salt is formed  $= \text{C} \left\{ \begin{array}{l} (\text{SO}_3\text{K})_3 \\ \text{SH} \end{array} \right\} + 2\text{H}_2\text{O}$ , forming clear triclinic crystals.

The hydrogen which in this salt is combined directly with sulphur in the SH residue, the author endeavoured to replace by mercury, but without success.

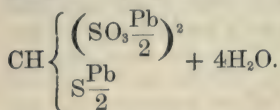
The free acid, obtained by precipitating a solution of the potassium salt with basic lead acetate, decomposing this with sulphuretted hydrogen, and evaporating over sulphuric acid *in vacuo*, formed a thick syrupy liquid, which very quickly decomposed in the air.

With ferric chloride this acid gives a deep blue coloration.

No other salt was prepared satisfactorily.

2. If the precipitate, obtained by adding basic lead acetate to a solution of the above potassium salt, be washed, boiled with dilute

acetic acid, and filtered, the filtrate deposits, on cooling, small needle-shaped crystals, which gave numbers corresponding to the formula

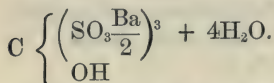


This is the lead salt of the *disulpho* acid =  $\text{CH} \left\{ \begin{array}{l} (\text{SO}_3\text{H})_2 \\ \text{SH} \end{array} \right\}$ .

A potassium salt has also been obtained, to which the formula  $\text{CH} \left\{ \begin{array}{l} (\text{SO}_3\text{K})_2 \\ \text{SH} \end{array} \right\} + \frac{1}{2}\text{H}_2\text{O}$  is assigned. The free acid was obtained, but always associated with a little potassium salt. With barium chloride and lead acetate, it gives flocculent precipitates, being thus distinguished from the *trisulpho* acid.

3. If bromine be slowly added to a solution of potassium methylmercaptan trisulphate, a new salt crystallises out, on cooling the solution, in colourless needles, having the formula  $\text{C} \left\{ \begin{array}{l} (\text{SO}_3\text{K})_3 \\ \text{OH} \end{array} \right\} + \text{H}_2\text{O}$ , the residue, HS, of the trisulpho-acid being changed by the action of bromine to hydroxyl, HO. The watery solution of this salt gives with barium chloride tolerably large leaf-like crystals of an insoluble barium salt; no colour with ferric chloride.

The free acid, = methylalcohol-trisulphonic acid, was obtained as a thick syrup, yielding crystals on further evaporation over sulphuric acid *in vacuo*. An ammonium salt  $\text{C} \left\{ \begin{array}{l} (\text{SO}_3\text{NH}_4)_3 \\ \text{OH} \end{array} \right\}$ , also a barium salt



A mercury salt, and a silver salt, were prepared, as also a salt to which the formula  $2\text{C} \left\{ \begin{array}{l} (\text{SO}_3\text{K})_3 \\ \text{OH} \end{array} \right\} + \text{C} \left\{ \begin{array}{l} (\text{SO}_3\text{K})_3 \\ \text{O} \frac{\text{Pb}}{2} \end{array} \right\} + 3\text{H}_2\text{O}$  is given. This acid likewise gives a double lead salt with lead acetate.

4. By acting on sulphocarbonyl chloride,  $\text{CSCl}_2$  with potassium sulphite, a salt is obtained exactly agreeing with the salt prepared from  $\text{CSCl}_4$ , viz., potassium methylmercaptantrisulphate,  $\text{C} \left\{ \begin{array}{l} (\text{SO}_3\text{K})_3 \\ \text{SH} \end{array} \right\} + 2\text{H}_2\text{O}$ .

5. By continued boiling of potassium sulphite with carbon disulphide, the same salt is produced.

M. M. P. M.

**Allylsulphonic Acid, and some of its Salts.** By A. V. RAD  
(Ann. Chem. Pharm., clxi, 218).

NEUTRAL potassium sulphite dissolved in a small quantity of water was boiled with its own weight of allyl iodide until the latter disappeared. The liquid, on evaporation on the water-bath, gave a crystalline residue, which was exhausted with boiling alcohol. On cooling, a white salt was obtained, which, after washing with alcohol, had the composition of a mixture of potassium iodide and allyl-sulphonate,  $7(\text{C}_3\text{H}_5\text{O}\cdot\text{SO}_2\text{K}) + 6\text{KI}$ . On addition of ether to the alcoholic mother-liquors, a salt of similar appearance was precipitated, which had the composition  $3(\text{C}_3\text{H}_5\text{O}\cdot\text{SO}_2\text{K}) + 2\text{KI}$ . On addition of lead acetate to the aqueous solution of these salts, lead iodide was precipitated; the filtrate decomposed by hydrogen sulphide, evaporated, extracted with alcohol, and precipitated with ether, furnished a salt not quite free from iodine; but a pure salt of composition  $\text{C}_3\text{H}_5\text{O}\cdot\text{SO}_2\text{K}$  was obtained by decomposing the double iodised compound with warm sulphuric acid, evaporation of most of the excess of acid, extraction with alcohol after neutralisation with potassium carbonate, and precipitation with ether; the product was white, indistinctly crystalline, and readily soluble in water.

The barium salt was a hygroscopic white mass, soluble in water and alcohol, but not in ether; the lead salt crystallised from alcohol in golden crystalline plates. The acid itself could not be obtained in a sufficient state of purity for analysis.

C. R. A. W.

**Preliminary Notice on Amidobenzene-sulphuric Acid.** By  
H. ROSE (Deut. Chem. Ges. Ber., v, 41—42).

A PECULIAR reaction on this acid is caused by the influence of copper chloride under certain conditions. Copper chloride alone is without action on an aqueous solution of this acid, but if whilst the liquid is boiling, ammonium chloride and a small quantity of ammonia be added, it becomes immediately of a dark red colour. On removing the copper by sulphuretted hydrogen, the colouring matter is reduced, and the solution becomes brown in colour. On allowing it to remain in contact with air, it is again oxidised, the surface becomes once more red, and on shaking, or on removing the sulphuretted hydrogen by warming, the original colour returns. On evaporation, the colouring matter is obtained. By the addition of a sufficient quantity of copper chloride, amidobenzene-sulphuric acid is completely decomposed. The colouring matter is easily dissolved by water and alcohol, which it colours intensely red; it is completely insoluble in ether and in benzene. It is destroyed by tin chloride and nitric acid; concentrated sulphuric acid dissolves it with a brown coloration; on diluting the solution, the characteristic red colour reappears.

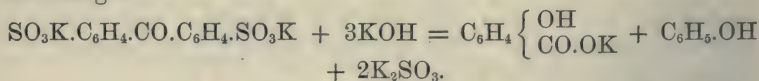
T. E. T.



**Benzophenone-sulphonic Acid.** By W. STAEDEL (Zeitschr. f. Chem., [2], viii, 553).

Cold sulphuric acid dissolves benzophenone without alteration, the addition of water reprecipitating the substance; if, however, the liquid be gently warmed, and best if fuming acid be employed, a sulphonic acid is formed, which yields a sparingly soluble anhydrous barium salt,  $C_{13}H_9O(SO_3)_2Ba$ , and readily soluble potassium and sodium salts; a small quantity of an uncrystallisable barium salt is also obtained, apparently an isomeride of the above crystalline *benzophenone-sulphonate of barium*.

On fusing the potassium salt with caustic potash, there are produced phenol in small quantity, paroxybenzoic acid in large quantity, and another acid more soluble than paroxybenzoic in small quantity. The paroxybenzoic acid exhibits all the properties of a pure sample of that substance when compared with it; it can be sublimed with a trace of decomposition, the sublimate containing a minute quantity of phenol, which lowers the melting point several degrees. The production of paroxybenzoic acid as principal product indicates that the  $SO_3H$  groups are in the 1·4 position with respect to the CO group, the decomposition being—



C. R. A. W.

**On Certain Acetal Derivatives.** By A. PINNER (Ber. Deut. Chem. Ges., v, 147).

ATTEMPTS to procure glycollic aldehyde,  $\begin{matrix} CH_2.OH \\ CHO \end{matrix}$ , by distillation of calcium glycollate and formate, gave an excessively small yield, the greater part of the glycollate being carbonised; in order to obtain larger quantities, acetal boiling at  $103^\circ$ — $105^\circ$  was treated with bromine, allowed to fall into it drop by drop, the mass being well cooled. On washing with water and alkalis to neutralise retained hydrobromic acid, a heavy slightly coloured oil is obtained, the vapour of which powerfully attacks the eyes and nostrils; by fractional distillation, *monobromacetal*,  $CH_2Br.CH \begin{Bmatrix} O.C_2H_5 \\ O.C_2H_5 \end{Bmatrix}$  is obtained, boiling at  $170^\circ$ , with slight decomposition. In the pure state it has a not unpleasant smell, and is insoluble in water. When it is treated with alcoholic potash for 12 hours, at  $160^\circ$ — $180^\circ$ , the bromine becomes replaced by hydroxyl, forming *glycolacetal*,  $CH_2.OH-CH \begin{Bmatrix} O.C_2H_5 \\ O.C_2H_5 \end{Bmatrix}$ , a colourless, pleasantly smelling liquid, boiling at  $167^\circ$ , without decomposition; vapour density found =  $66\cdot61$  ( $H = 1$ ); calculated = 67.

Concentrated sulphuric acid and gaseous hydrogen chloride completely destroy glycolacetal at common temperatures; glacial acetic acid has no action in the cold; at  $100^\circ$  action commences with slight browning, and at  $120^\circ$  the decomposition is complete in a few hours.

On distillation of the product from 50 grams of glycolacetal, agitation of the distillate with sodium hydrogen sulphite, and decomposition of the sulphite compound by soda and distillation, a liquid was obtained of weak aldehyde-like odour, and giving a silver mirror; the quantity was, however, too small to allow of the separation of the aldehyde-body; sulphuretted hydrogen yielded a few oily drops, with the characteristic smell of sulphaldehyde, but too little for investigation.

*Glycolacetal ether*,  $\text{CH}_2(\text{O}.\text{C}_2\text{H}_5)-\text{CH} \begin{Bmatrix} \text{O}.\text{C}_2\text{H}_5 \\ \text{O}.\text{C}_2\text{H}_5 \end{Bmatrix}$ , is an agreeably smelling liquid, boiling at  $164^\circ$ , without decomposition, obtained by the action of concentrated sodium alcoholate solution, at  $160^\circ$  on bromoacetal; it is entirely destroyed by strong acids. Similarly the *acetal corresponding to glyoxal*,  $\text{CH} \begin{Bmatrix} \text{O}.\text{C}_2\text{H}_5 \\ \text{O}.\text{C}_2\text{H}_5 \end{Bmatrix}-\text{CH} \begin{Bmatrix} \text{O}.\text{C}_2\text{H}_5 \\ \text{O}.\text{C}_2\text{H}_5 \end{Bmatrix}$ , is obtained by the action of sodium alcoholate on dichloroacetal; it boils at about  $180^\circ$  without decomposition, and is entirely destroyed by strong acids.

C. R. A. W.

**Contribution to the History of Chloral.** By C. BISCHOFF  
(Deut. Chem. Ges. Ber., v, 86—88).

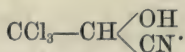
It would seem, from the researches of Liebig and Wöhler, of Baeyer and of Melms, that trigenic acids are formed by the action of cyanic acid on aldehydes, so that the production of these peculiar acids may be regarded as a criterion of an aldehyde. The author therefore passed the vapour of dry cyanic acid into chloral, hoping to obtain a trichlorinated trigenic acid. The vapour is readily absorbed by the chloral, which sometimes solidifies at the instant of saturation; at others, gas is evolved at a certain stage of the saturation, and the mixture solidifies to a vitreous mass, like fused borax, whilst at other times this change takes place only after standing some days. The product, however, in all instances, yields the same result when boiled with moderately concentrated hydrochloric acid, leaving a white granular powder, insoluble in water and hydrochloric acid. This, however, is readily soluble in hot alcohol, and even more so in ether, from which it crystallises in microscopic prisms having the composition  $\text{C}_5\text{H}_3\text{Cl}_6\text{NO}_3$ , and melting at  $167^\circ-170^\circ$ , with partial decomposition. Boiled with potassium hydrate, it yields chloroform, formic acid, carbonic acid, and ammonia, so that the constitution of the compound may be expressed thus:— $\text{CCl}_3.\text{CH} \begin{Bmatrix} \text{O} \\ \text{O} \end{Bmatrix} \text{C} \begin{Bmatrix} \text{HN} \\ \text{O} \end{Bmatrix} \text{CH}.\text{CCl}_3$ , two chloral molecules being united by cyanic acid. On heating it to  $200^\circ$ , it splits up, chloral distilling over, and cyamelide being formed. It dissolves readily in alcoholic ammonia, and after the removal of the excess of the latter, silver nitrate gives a precipitate of silver cyanate. The hydrochloric acid solution of the crude substance, after the separation of the compound above described, yielded on evaporation, besides ammonium chloride, two distinct crystalline compounds, the quantity of which, however, was so small that the author has not been able to investigate them accurately.

C. E. G.

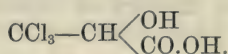
**Chloral-Cyanhydrate and Trichlorolactic Acid.**

By C. BISCHOFF and A. PINNER (Deut. Chem. Ges. Ber., v, 113).

By the action of hydrochloric and hydrocyanic acids on chloral, Städeler obtained a syrupy liquid, resembling lactic acid, but carried his experiments no further. The authors in re-examining this reaction, have obtained a compound of chloral and hydrocyanic acid, by simply digesting the two substances together in aqueous solution. Chloral-cyanhydrate forms cauliflower-like masses of colourless prisms, having a penetrating bitter taste. It is easily soluble in water, in alcohol, and in ether. The numbers obtained by analysis correspond with the formula—



When this substance is digested with moderately strong hydrochloric acid, it furnishes ammonium chloride, and a crystallisable acid, which was identified with trichlorolactic acid. †



The authors are carrying on the investigation of this body and its salts, and are about to extend their experiments to the croton-chloral.

W. A. T.

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**The Oxidation of the Ketones as a Means of Determining the Constitution of Acids and Alcohols.** By A. POPOFF (Deut. Chem. Ges. Ber., v, 38—41).

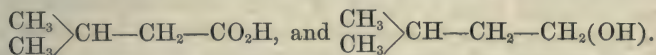
THE author first refers to a previous memoir, in which he compares the results obtained by himself and Kolbe, Wurtz, Erlenmeyer, Wanklyn, and Buttlerow, from the oxidation of the ketones, and of the secondary and tertiary alcohols. When ketones are taken in which one of the alcohol-radicals (R in the following general formulæ) united to the carbonyl group is phenyl, methyl, or in some cases ethyl,

1.  $\text{CH}_3\text{—}(\text{CH}_2)_n\text{—CO—R}$
2.  $\text{—CH}_2\text{—}(\text{CH}_2)_n\text{—CO—R}$
3.  $\text{—CH—CO—R}$
4.  $\text{≡C—CO—R,}$

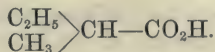
then, on oxidation, the carbonyl and this alcohol-radical invariably remain united, whilst the other alcohol-radical becomes oxidised. If this latter is the radical of a normal alcohol, it yields a normal acid; if it is an iso-alcohol radical, an iso-acid is produced; a secondary alcohol gives an acetone; whilst a tertiary alcohol suffers decomposition. In order to prove the applicability of this method of determining the constitution of the acids, and consequently of their corresponding alcohols, the author has studied the reactions of the phenyl-ketone from the valerianic acid obtained from fermentation amyl alcohol. The amyl alcohol boiled at  $130^\circ\text{—}131.5^\circ$ , and had a rotation power,  $\alpha = -2.4^\circ$ ; the valerianic acid obtained from it boiled at  $174^\circ\text{—}176^\circ$ ; its



rotation power was  $\alpha = +4.4^\circ$ . It consisted therefore in great part of the inactive acid, a small portion only of the active modification being present. The calcium salt of this acid was intimately mixed with an equivalent amount of calcium benzoate, and distilled in small portions at a time. The greater portion of the product boiled at  $224^\circ$ — $228^\circ$ ; a smaller quantity boiling at  $228^\circ$ — $233^\circ$ . On rectifying the 225—226 fraction, it yielded on analysis numbers agreeing with the composition of butyl-phenyl-ketone. The portion boiling at  $231.5^\circ$ — $232^\circ$  showed an increased amount of carbon, and a diminution of hydrogen, due probably to benzophenone. The true boiling point of iso-butyl-phenyl ketone would appear to be  $225.5^\circ$ . On oxidation this product yielded—1. Benzoic acid (melting point,  $121.5^\circ$ ) analysis of silver-salt gave 47.22 per cent. aq.; calculated, 47.16. 2. Iso-butyric acid. The calcium salt prepared from this acid gave the characteristic long, transparent, efflorescent needles. On drying, the salt lost 29.28 per cent. water; isobutyrate of calcium contains 29.6 per cent. On warming a concentrated solution of the normal calcium butyrate, the salt is precipitated in shining leaflets, but not the slightest turbidity was observed on warming the iso-butyrate of calcium obtained by the author. The silver-salt crystallised in thin rectangular tables; analysis proved that it contains the theoretical amount of silver carbon and hydrogen. In addition to these acids a minute quantity of acetic acid was detected. By fractional precipitation, an impure silver acetate was obtained. The formation of benzoic acid shows that the carbonyl and phenyl groups remain united in the butyl-phenyl ketone. The production of iso-butyric acid proves that iso-butyl was present in the ketone, and therefore in the valerianic acid and in the amyl alcohol. Since the valerianic acid employed consisted mainly of the inactive modification, and since isobutyric acid was produced in quantity, it follows that the inactive valerianic acid, and the inactive amyl alcohol contain isobutyl—



This result confirms the conclusions of Erlenmeyer, Frankland and Duppa, and Buttlerow, respecting the constitution of fermentation amyl alcohol. The author leaves it undecided whether the acetic acid is due to impurity in the product, or to a secondary and irregular oxidation of the ketone, or to the presence of the small quantity of the active valerianic acid. This possibly may be ethyl-methyl-acetic acid,



In this case its ketone would certainly yield acetic acid.

T. E. T.

**Transformation of Acetone into Hydride of Hexylene (Di-propyl).** By G. BOUCHARDAT (Compt. rend., lxxiv, 809—811).

PINACONE,  $\text{C}_6\text{H}_{14}\text{O}_2$ , which is formed by the action of nascent hydrogen upon acetone, boiled with iodine and phosphorus in presence of water,

or heated in sealed tubes with hydriodic acid, yields a mixture of pinacone,  $C_6H_{12}O$  (anhydride of pinacone), an iodide,  $C_6H_{11}I$ , (b. p.  $142^\circ$ — $145^\circ$ ), which constitutes three-fourths of the crude product, and small quantities of more condensed derivatives of acetone.

The iodide obstinately retained nearly 1 per cent. of oxygen, and therefore, that no doubt of its composition might remain, a portion was treated with zinc and hydrochloric acid. A hydrocarbon was thus obtained which combined with bromine to form  $C_6H_{12}Br_2$ , without disengagement of hydrobromic acid.

The iodide,  $C_6H_{11}I$ , heated with hydriodic acid gave, besides a little inflammable gas and several liquid hydrocarbons boiling about  $130^\circ$ , a liquid, the boiling point of which was  $59^\circ$ , and vapour density 2.947. Analysis gave numbers corresponding to the formula  $C_6H_{14}$ ; it is therefore the hydride of dipropylene already obtained by Berthelot by treating diallyl with hydriodic acid, and isomeric with the hydride of hexylene, which is obtained by hydrogenating benzene, and boils  $10^\circ$  higher.

Iododipropylene is rapidly attacked by bromine, with disengagement of hydrobromic acid and liberation of iodine. The body formed is crystallisable, and fuses at  $142^\circ$ . It sublimes below its fusing point in irritating vapours. It is a bromide of bromodipropylene,  $C_6H_{10}Br_4$ , isomeric with diallyl tetrabromide, from which it is distinguished by well-marked characters, including fusing point and crystalline form.

W. A. T.

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**Derivatives of Butyrene.** By C. M. KURTZ (Ann. Chem. Pharm., clxi, 205).

PURE butyric acid was converted into calcium salt, and distilled in quantities of 10—20 grms. at a time. About 400 c.c. of crude distillate was obtained from a pound of acid. After separation of the aqueous portion, crystals were obtained on agitation with a strong solution of acid sodium sulphite; on decomposition by sodium carbonate, these furnished a liquid boiling entirely between  $75^\circ$  and  $105^\circ$ , probably a mixture of methyl-ethyl ketone and methyl-propyl ketone. Saturation of the crude butyrene with ammonia gas, and then with sulphur dioxide, also failed to produce a crystalline butyrene compound; whence the author considers that there are grounds for Grimm's conclusion that only those ketones yield crystals with acid sulphites that contain the methyl group.

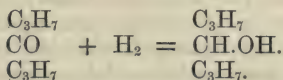
By fractional distillation, a body of composition  $C_7H_{14}O$  was isolated, boiling at  $139^\circ$ — $144^\circ$ , and having all the properties of Chancel's butyrene, which boiled at  $144^\circ$ . A few drops came over between  $75^\circ$  and  $125^\circ$ , and a small quantity at  $200^\circ$ . On oxidation by potassium dichromate and sulphuric acid, the butyrene thus obtained yielded propionic and butyric acids, whence, according to Popoff's results, its formula

must be  $CO \begin{cases} C_3H_7 \\ C_3H_7 \end{cases}$

On heating butyrene with nitric acid, a vigorous reaction took place, and a heavy oily fluid was produced, which on addition of alcoholic potash gave a crystalline mass of the potassium salt of an acid, having

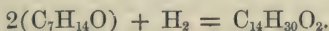
the percentage composition of nitropropionic acid,  $\text{C}_3\text{H}_4(\text{NO}_2)\text{KO}_2 + \text{H}_2\text{O}$ . By similar means the ammonium salt was obtained; this, with hydrogen sulphide, yielded small crystals which did not appear to be alanine, as they were readily soluble in cold water and alcohol. Silver nitrate gave with the potassium salt a yellow crystalline precipitate, which exploded below  $100^\circ$ . Chancel's former results (Chancel, *Ann. Chem. Pharm.*, lii, 295; Chancel and Laurent, *ibid.*, lxiv, 331) differed in many respects from the author's. At first he considered the acid to be nitrobutyric; later, nitropropionic. He described the silver salt as a basic salt containing crystallisation-water, and decomposed on boiling into silver oxide and neutral silver salt.

On addition of sodium in small pieces to butyrene mixed with a very little water, a vigorous reaction took place; the resulting product contained butyrene-pinacone, and a liquid boiling at  $149^\circ$ — $150^\circ$ , formed by the reaction—



This was sparingly soluble in water, but readily in all proportions of alcohol. By oxidation with potassium dichromate and sulphuric acid, it furnished butyrene. The fact that the boiling point is some  $14^\circ$  lower than heptyl alcohol\* from petroleum (Schorlemmer), and its mode of formation, induce the author to term this substance *pseudobutyl alcohol*. Treatment with iodine and phosphorus furnished a *pseudo butyl iodide* of sp. gr. 1.2 at  $20^\circ$ , and boiling with partial decomposition at  $180^\circ$ .

The butyrene-pinacone was a solid crystalline body melting at  $68^\circ$ , solidifying at  $57^\circ$ , and of sp. gr. 0.87 at  $20^\circ$ . It distilled at about  $260^\circ$ , and by oxidation with sulphuric acid and potassium dichromate, it re-produced butyrene. Its formation is given by the equation—



Chlorine acts on butyrene with evolution of hydrogen chloride, producing a liquid which decomposes on distillation or on standing. A similar product is obtained with potassium chlorate and hydrochloric acid. Phosphorous chloride also acts readily, but the product could not be satisfactorily separated from phosphorus oxychloride.

C. R. A. W.

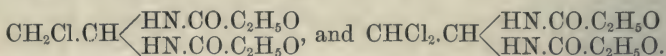
### Action of Chlorine and Bromine on an Alcoholic Solution of Hydrocyanic Acid. By C. BISCHOFF (*Deut. Chem. Ges. Ber.*, v, 80—86).

THE author, on repeating Stenhouse's experiment (*Ann. Chem. Pharm.*, xxx, 93) of passing chlorine into an alcoholic solution of hydrocyanic

\* Note by Abstractor.—Schorlemmer (*Ann. Chem. Pharm.*, clxi, 273) finds that the normal alcohol boils at  $170^\circ$ — $178^\circ$ , or about  $24^\circ$  higher than this pseudo-alcohol; while the secondary alcohol,  $\text{CH} \begin{cases} \text{CH}_3 \\ \text{OH} \\ \text{C}_5\text{H}_{11} \end{cases}$ , boils at  $160^\circ$ — $162^\circ$ , or about  $12^\circ$  higher.



acid, frequently obtained the monochlorinated compound  $C_8H_{15}ClN_2O_4$ , corresponding to Stenhouse's dichlorinated compound  $C_8H_{14}Cl_2N_2O_4$ . It is very similar to the latter, but crystallises in longer and larger needles, which melt at  $147^\circ$ . When chlorine is passed into an alcoholic solution of mercury cyanide, the dichlorinated compound is generally obtained. The monochloro-compound when treated with a solution of potassium hydrate, gives a distillate of alcohol, water, and ammonia, potassium chloride and carbonate remaining behind, whilst with alcoholic ammonia at  $150^\circ$  it yields a mixture of organic bases which the author has not investigated. Digested with hydrochloric acid for 24 hours at  $100^\circ$ , it forms ethyl chloride and carbonic acid which escape on opening the tubes, and chlorhydrin and other glycol-compounds, which remain dissolved in the aqueous hydrochloric acid. From the decomposition of this substance the author believes its formation to take place in the following way:—It is well known that chlorinated acetals are formed by the action of chlorine on aqueous alcohol, and that urethane is produced by cyanogen chloride under similar circumstances, so that when both reactions take place simultaneously, compounds are formed containing the urethane residue combined with the chlorinated ethylidene group in place of the alcohol residue (ethoxyl) in chlorinated acetal—



This view of their constitution readily accounts for their splitting up into alcohol, carbonic acid, and ammonia, and also for the formation of glycol compounds. The attempts to obtain the corresponding compounds in other series were fruitless, chlorinated acetones and methyl-urethane being obtained with methyl alcohol, whilst amyl alcohol yielded amyl urethane. When a slight excess of bromine is added to an alcoholic solution of hydrocyanic acid, and the mixture is gently heated, a violent reaction ensues, cyanogen bromide volatilising, and ammonium bromide separating from the solution. On addition of water, an oil separates, which consists chiefly of a solution of the bromine compound in ethyl bromide, and leaves the former on being allowed to evaporate spontaneously. The author only once obtained the monobrominated compound  $C_8H_{15}BrN_2O_4$ , which melts at  $142^\circ$ , and crystallises in larger needles than the easily prepared dibrominated compound. The dibrominated compound  $C_8H_{14}Br_2N_2O_4$  melts at  $115^\circ$ — $116^\circ$ , and crystallises from ether in long needles. Iodine, alcohol, and hydrocyanic acid gave a negative result, as did also the digestion of the bromine compound with potassium iodide. Neither the chlorine nor the bromine compounds are altered by the action of nascent hydrogen.

C. E. G.

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**Derivatives of Fulminic Acid.** By E. SELL and R. BIEDERMANN (Deut. Chem. Ges. Ber., v, 89).

By adding iodine in small portions to fulminating mercury covered with ether, di-iodonitroacetonitrile,  $C(CN)(NO_2)I_2$ , is formed, which

crystallises from the ethereal solution in colourless monoclinic prisms, melting with partial decomposition at  $86^{\circ}$  to a red liquid, and decomposing completely at  $170^{\circ}$ . Iodine, therefore, simply replaces the mercury in the fulminate. Bromine, as Kekulé has shown, acts in a similar way, but, besides dibromonitroacetonitrile, bromopierin is also formed, whilst chlorine eliminates both the mercury and the cyanogen, with formation of chloropierin.

C. S.

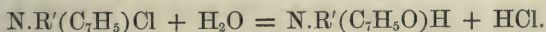
### Action of Phosphorus Pentachloride on certain Aciamides.

By ANNA WOLKOFF (Ber. Deut. Chem. Ges. v, 139).

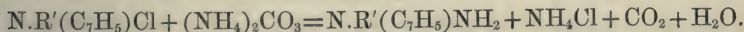
THE authoress applies the term *aciamide* to bodies which, though formed on the ammonia type, yet possess acid characters, such as the benzoyl-sulphotoluolamides obtained by the action of benzoyl chloride on  $\alpha$  and  $\beta$  sulphotoluolamides, and the analogous bodies previously described by her, derived from nitrosulphotoluolamide,  $\alpha$ -sulphonaphthalenamide, sulphoxylolamide, and sulphocymolamide, by the substitution of the benzoyl group for hydrogen (*Zeitschr. f. Chem.* 1870, p. 321 and 577). Her present researches show that the action of pentachloride of phosphorus on all these bodies may be expressed by the following general equation in which R' indicates the sulphonic acid radical—



With water the resulting chlorides decompose, reproducing the original aciamides—



With ammonium carbonate they form the corresponding amides, thus—



Hence the conclusion is drawn that whereas the sulphonic amides possess alcoholic characters, when one of the hydrogens of the amidogen group becomes replaced by an acid radical (*e.g.*, benzoyl), the other hydrogen acquires metallic characters, *i.e.*, those of the basic hydrogen in a monobasic acid.

The following chlorides from aciamides are described :—

*Benzoylsulphobenzolaciamide Chloride*,  $\text{N(C}_6\text{H}_5\text{SO}_2\text{)(C}_7\text{H}_5\text{)Cl}$ .—Previously obtained by Gerhardt, whose results, however, were not confirmed by Wichelhaus. Crystallisable from ether; melting point  $73^{\circ}$ — $75^{\circ}$ .

*Benzoylsulphotoluolaciamide Chloride*,  $\text{N(C}_7\text{H}_7\text{SO}_2\text{)(C}_7\text{H}_5\text{)Cl}$ .—From benzoyl- $\alpha$ -sulphotoluolaciamide. Crystallisable from ether; melting point  $100^{\circ}$ . The amide from this chloride crystallises from alcohol, melts at  $140^{\circ}$ , is insoluble in water, aqueous ammonia and alkaline carbonates; aqueous caustic alkalies slowly dissolve it with evolution of ammonia.

*Benzoyl- $\alpha$ -nitrosulphotoluolaciamide Chloride*,  $\text{N[C}_7\text{H}_6\text{(NO}_2\text{)SO}_2\text{]}$

$(C_7H_5)Cl$ .—Crystallisable from boiling ether, in which it is difficultly soluble; melts at  $125^\circ$ . The amide melts at  $122^\circ$ — $123^\circ$ , and behaves like the foregoing amide.

*Benzoylsulphocymolaciamide Chloride*,  $N(C_{10}H_{13}SO_2)(C_7H_5)Cl$ .—Soluble in ether but not crystallisable, being left as a thick oily fluid on evaporation; the amide melts at  $188^\circ$ .

*Benzoyl- $\alpha$ -sulphonaphthalenaciamide Chloride*,  $N(C_{10}H_7SO_2)(C_7H_5)Cl$ .—Crystallisable from ether; melts at  $92^\circ$ — $94^\circ$ ; the amide is crystalline.

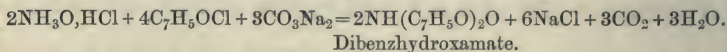
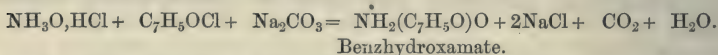
These chlorides are not identical with the compounds of nitriles and oxychlorides previously known; equivalent quantities of benzonitrile and  $\alpha$ -sulphotoluol-chloride were heated together in a sealed tube to  $110^\circ$ — $115^\circ$  for weeks without entering into combination or undergoing any change.

C. R. A. W.

### The Benzoyl Derivatives of Hydroxylamine. By W. LOSSEN (Ann. Chem. Pharm. cxii, 347—362).

THE hydrogen of hydroxylamine can be replaced by benzoyl, giving an indifferent body, tribenzhydroxylamine, and two acids, which the author proposes to rename benzhydroxamic and dibenzhydroxamic acids, like the corresponding oxatyl compounds.

*Preparation of Benzhydroxamic and Dibenzhydroxamic Acid*.—Heating dry hydroxylamine hydrochloride, or a solution of it, in a hydrocarbon boiling at about  $110^\circ$ , with benzoyl chloride, is difficult and yields but little of the product. If, however, benzoyl chloride be poured into an aqueous solution of hydroxylamine or its hydrochloride supersaturated with soda, it is almost entirely converted into benz- and dibenz-hydroxamic acid,



The two acids are produced simultaneously. 1 part of hydroxylamine salt is dissolved in 8 to 10 parts of water with sufficient soda to take up all the chlorine of the reaction, and 3 parts benzoyl chloride are added gradually with constant agitation, keeping the mixture cold. The sparingly soluble dibenzhydroxamic acid which separates should be recrystallised from alcohol, while benzhydroxamic acid, which remains for the most part in solution, may be obtained by precipitating with baryta water, decomposing with sulphuric acid, and purifying the product by crystallisation from a small quantity of warm alcohol, and washing the crystals with ether. The hydroxylamine solution may be obtained by digesting tin for a week in the cold with nitric acid, hydrochloric acid, and water, and precipitating the tin with soda.

*Benzhydroxamic Acid*,  $NH_2(C_7H_5O)O$ .—The pure acid crystallises in colourless rhombic plates, soluble in 44.5 parts of water at  $6^\circ$ , and much more easily in warm water, very soluble in alcohol, little in



ether or carbon disulphide, and not at all in benzol. The impure acid forms warty masses. It has an acid reaction and melts at  $124.5^{\circ}$ . The acid and its salts are decomposed more or less violently at a high temperature. Heated with dilute hydrochloric or sulphuric acid it splits up into benzoic acid and a salt of hydroxylamine.

Benzhydroxamic acid is monobasic, yet, like oxalhydroxamic, it has a tendency to form acid salts. The acid potassium salt,  $\text{NH}(\text{C}_7\text{H}_5\text{O})\text{OK} + \text{NH}_2(\text{C}_7\text{H}_5\text{O})\text{O}$ , and the acid sodium salt,  $\text{NH}(\text{C}_7\text{H}_5\text{O})\text{ONa} + \text{NH}_2(\text{C}_7\text{H}_5\text{O})\text{O} + 3\text{H}_2\text{O}$ , form rhombic prisms or plates, moderately soluble in warm water, little soluble in alcohol. The sodium salt effloresces in dry air. An alcoholic solution of the free acid treated with potash gives a precipitate of the acid salt, redissolved by further addition, but reappearing in crystals as the solution evaporates in air.

The neutral barium salt is obtained in microscopic needles when the acid potassium salt, neutralized with ammonia, is treated with barium chloride. If the ammonia be omitted a variable mixture of neutral and acid barium salt is precipitated. The latter crystallises in small prisms along with the free acid, when the neutral salt is decomposed with insufficient sulphuric acid and the filtrate allowed to evaporate. It is nearly insoluble in water and alcohol. The calcium and zinc salts are neutral: the former is an amorphous, the latter a crystalline precipitate.

Solutions of the acid sodium salt give white precipitates with manganous chloride, cadmium sulphate, alum and lead nitrate, nearly white with cupric sulphate, green with chrome alum, whitish green with nickel sulphate, peach-coloured with cobalt nitrate, yellow with mercuric chloride, all soluble in excess; white with silver nitrate, rapidly blackening, and insoluble in excess. Ferric chloride gives a dark red precipitate, soluble with intense red colour in excess or in dilute sulphuric or hydrochloric acid. The latter when concentrated destroys the colour, but it appears again on dilution.

*Dibenzhydroxamic Acid*,  $\text{NH}(\text{C}_7\text{H}_5\text{O})_2\text{O}$ , crystallises by cooling in needles or prisms, by spontaneous evaporation of the alcoholic solution in shining rhombic crystals. It dissolves with difficulty in water, cold alcohol, ether, or carbon disulphide, more easily in hot alcohol, not at all in benzol. It has an acid reaction, melts at  $145^{\circ}$ , decomposes violently at a higher temperature with formation, among other products, of benzanilide. With acids it splits up like benzhydroxamic acid, with alkalis it gives a benzoate and a benzhydroxamate. The latter by shaking with benzoyl chloride and water may be reconverted into dibenzhydroxamic acid.

The acid is monobasic and forms neutral salts. The potassium salt,  $\text{N}(\text{C}_7\text{H}_5\text{O})_2\text{OK}$ , crystallises from alcohol in pearly, very thin plates or microscopic six-sided tables, decomposing with violence by heat, and leaving a benzoate and a sparingly soluble indifferent body. The aqueous solution decomposes on standing, without, however, producing benzhydroxamic acid. The sodium salt is rather more soluble in alcohol than the potassium salt, and forms stout-pointed prisms.

A fresh solution of potassium dibenzhydroxamate gives white precipitates with manganous chloride, with lead, silver, and cobalt nitrates, and with zinc and cadmium sulphates; blue-green with chrome alum;

apple-green with nickel sulphate, and with ferric chloride a reddish-yellow precipitate but no coloration. It is distinguished from benzhydroxamate and oxalhydroxamate by giving no precipitate with salts of the alkaline earths.

*Tribenzhydroxylamine*,  $N(C_7H_5O)_3O$ , is among the products of the action of a solution of benzoyl chloride in a hydrocarbon boiling at  $110^\circ$ , on dry hydroxylamine hydrochloride. It is also formed by heating potassium dibenzhydroxamate to  $100^\circ$  with benzoyl chloride in excess, afterwards removing the benzoyl chloride with ether and the potassium chloride with water, and recrystallising the residue from alcohol. It is insoluble in water, ether, and benzol, nearly insoluble in cold, but easily soluble in boiling alcohol, from which it crystallises in groups of shining prisms. It melts at  $141^\circ$  and decomposes at  $190^\circ$ . Its alcoholic solution treated with potash splits up into benzoate and dibenzhydroxamate.

In conclusion, although tribenzhydroxylamine admits probably of only one rational formula, the acids each admit of two: the first may be  $NH(C_7H_5O)(HO)$  or  $NH_2(OC_7H_5O)$ , the second  $N(C_7H_5O)_2(HO)$  or  $NH(C_7H_5O)(OC_7H_5O)$ . Further researches must decide between them.

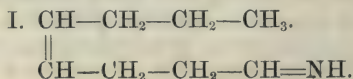
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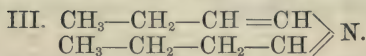
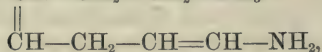
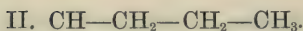
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**Artificial Conine.** By H. SCHIFF (Deut. Chem. Ges. Ber., v, 42—44).

ABOUT  $\frac{1}{4}$  kilo. butyraldehyde was mixed with an alcoholic solution of ammonia, and placed in sunshine during the summer months. Instead of the separation with platinum chloride, as described in his former communication, Schiff now finds it more convenient to separate the alcohol, ammonia, and unaltered butyraldehyde by distillation, then to heat the brown syrupy residue for a day to  $130^\circ$ — $150^\circ$ , and distil off the volatile portion in a current of steam. The tarry residue is then heated in sealed tubes to  $200^\circ$ , and again distilled in steam.

In the oily distillate the basic portion is removed by hydrochloric acid, decomposed by potash, and separated by repeated distillation in a stream of hydrogen. A portion boiling at  $166^\circ$ — $170^\circ$  is gradually obtained, and a second boiling at  $175^\circ$ — $195^\circ$ , and a third between  $205^\circ$ — $215^\circ$ . The greater portion of the first fraction boils at  $168^\circ$ , and has the composition and properties of natural conine. It acts as a violent poison, and with all the characteristic effects of the natural base. The sp. gr. is 0.893—0.899 at  $15^\circ$ . The artificial conine appears, however, to be only isomeric with the natural alkaloid. It shows slight differences in its behaviour towards silver nitrate, hydrochloric acid, and chloride of gold. Its coefficient of expansion is greater, and its solubility in water less, than that of natural conine. Moreover the artificial alkaloid is without action on polarised light. The author has proposed the following formulæ, the first of which he believes is possessed by natural conine:—

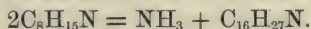




The behaviour of the synthetical base towards cenanthol and iodide of ethyl has shown that it contains no replaceable hydrogen. On warming with cenanthol, no separation of water occurs, and with iodide of ethyl the iodide of an ammonium base is obtained, the oxide of which is a strongly alkaline, bitter, easily decomposed, syrupy liquid. Artificial conine has therefore the formula III.

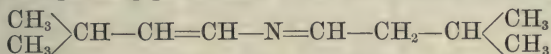
Dibutyraldine,  $\text{C}_8\text{H}_{17}\text{NO}$ , is therefore not identical with conhydrin. The author proposes to call the artificial base "paraconine."

The portion boiling above  $200^\circ$  contains the base  $\text{C}_{16}\text{H}_{27}\text{N}$ ; derived from tetrabutyraldine,  $\text{C}_{16}\text{H}_{29}\text{NO}$ . It is formed also in small quantity by the distillation of paraconine, thus:—



It boils at  $210^\circ$ , and has a sp. gr. of 0.915 at  $15^\circ$ .

The base  $\text{C}_{10}\text{H}_{19}\text{N}$ , obtained by Ljubavin from valeraldehyde, is doubtless the corresponding paraconine. Its constitution formula is—



The author thinks that the tetra-base may exist among the products of the reaction, and he considers that in all probability the optically active valeraldehyde would give a homologue of natural conine.

T. E. T.

**Facts relating to Diphenylamine.** By C. GIRARD and G. DE LAIRE (*Compt. rend.*, lxxiv, 811—813).

CONTRARY to the opinion expressed by Dusart and Bardy (*Compt. rend.*, 27th Nov., 1871), the authors find that pure aniline hydrochloride may be partly converted into diphenylamine by simply heating to  $300^\circ$ — $340^\circ$ , without the intervention of phenyl chloride.

The authors have also been unsuccessful in obtaining diphenylamine, as described by Dusart and Bardy, by heating dry sodium sulphophenate with aniline, except when a small quantity of a salt of aniline is present. When this is the case, the formation of diphenylamine results from the action of the aniline salt upon the aniline itself according to a well-known and admitted reaction. Similarly the production of diphenylamine by the action of iodide or bromide of phenyl on aniline occurs only when this iodide or bromide contains a trace of free acid, or the aniline a salt of aniline.

Further, contrary to MM. Dusart and Bardy, no benzonitrile was obtained by the authors on heating together sodium sulphophenate and potassium cyanide. The distillate consisted wholly of phenol.

And lastly, Dusart and Bardy having stated that by heating together phenol, ammonia hydrochloride, and hydrochloric acid they obtained diphenylamine, Girard and de Laire have repeated the experiment,



employing, however, for sake of simplicity, phenyl chloride itself instead of the mixed phenol and hydrochloric acid. Under these circumstances no reaction could be detected, and the whole of the phenyl chloride was recovered unchanged. W. A. T.

**A Third Nitraniline.** By J. FR. WALKER and TH. ZINCKE (Deut. Chem. Ges. Ber., v, 114—117).

OF the three nitranilines possible according to Kekulé's theory of the aromatic compounds, two only are at present known. The one results from the nitration of anilides, the other from the reduction of dinitrobenzene. The authors have succeeded in producing the third by taking as their starting point the  $\gamma$  bromonitrobenzene of Hübner and Alsberg. The transformation was effected by heating the substance for some hours to  $180^{\circ}$ — $190^{\circ}$ , with concentrated alcoholic solution of ammonia. The solution was then evaporated to dryness, and the nitraniline crystallised from water. By this process, whilst  $\alpha$ -bromonitrobenzene furnished a nitraniline identical with that discovered by Arppe, and afterwards produced from acetanilide by Hofmann, the second modification of bromonitrobenzene (melting point  $37^{\circ}$ — $38^{\circ}$ ) yielded a nitraniline differing from the two already known, and designated by the authors as metanitraniline.

It is distinguished by its solubility, melting point, and the colour of its salts. In water and in alcohol it is far more soluble, and the solutions are intensely yellow, and communicate this colour to the skin. With water-vapour it volatilises more easily than the two other modifications, and the watery distillate is coloured strongly yellow. The melting point of the base crystallised from water is  $66^{\circ}$ . By heating between two watch-glasses it yields a sublimate of oily drops, which become crystalline. Like the two other nitranilines, it forms salts of small stability, which, however, are not colourless, but distinctly yellow.

The authors have also succeeded in converting the bromonitrobenzene of Hübner and Alsberg (melting point  $37^{\circ}$ — $38^{\circ}$ ) into the volatile nitrophenol by heating with alkali.

In the following table the terms ortho-, meta-, and para-series are to be understood in their original sense, and not as indicating the positions 1 : 2, 1 : 3, 1 : 4:—

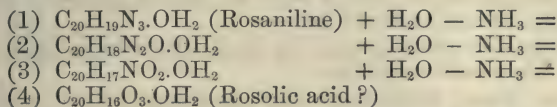
Ortho-series.	Meta-series.	Para-series.
$\alpha$ -Bromonitrobenzene. Melting point $125^{\circ}$ .	$\gamma$ -Bromonitrobenzene. Melting point, $37^{\circ}$ — $38^{\circ}$ . (Hübner and Alsberg.)	$\beta$ -Bromonitrobenzene. Melting point, $56^{\circ}$ . (Griess.)
$\alpha$ -Bromaniline, from Acetanilide.	$\gamma$ -Bromaniline. (Hübner and Alsberg.)	$\beta$ -Bromaniline. (Griess.)
Nitraniline, from Acetanilide.	Metanitraniline.	Paranitraniline.
Melting point, $146^{\circ}$ .	Melting point, $66^{\circ}$ .	Melting point, $108^{\circ}$ .
Orthonitrophenol.	Nitrophenol.	Unknown.
Melting point, $110^{\circ}$ .	Melting point, $45^{\circ}$ .	
Dibromobenzene.		Dinitrobenzene.
Melting point, $89^{\circ}$ .		

In the preparation of bromonitrobenzene the authors have ascertained that the formation of the  $\gamma$  modification, which formed the starting point of these experiments, is favoured by effecting the nitration of the bromobenzene at a temperature of  $90^{\circ}$ — $95^{\circ}$ .

W. A. T.

**New Mode of Decomposition of Rosaniline.** By C. LIEBERMANN (Deut. Chem. Ges. Ber., v, 144).

WHEN rosaniline, or better, its hydrochloride, is heated in a sealed tube with water to  $220^{\circ}$ , scarcely any action takes place; but after several hours at  $235^{\circ}$  a decomposition is produced which may be represented as the replacement of imidogen,  $\text{NH}$ , by  $\text{O}$ .



The products (2) and (3) are readily isolated; the aqueous liquid obtained deposits on evaporation beautiful red crystals, of the compound (3). This behaves as a weak acid, is soluble in ammonia, and reprecipitated by acids, the precipitate being considerably soluble in excess of hydrochloric acid. Reducing agents convert it into a colourless body.

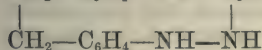
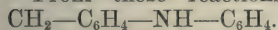
The solid contents of the tube, after washing with cold water, are treated with boiling water; substance (2) then dissolves, forming red crystalline needles resembling rosaniline on cooling; this body behaves as a base, and is but sparingly soluble in ammonia. It melts at  $176^{\circ}$  in a little tube, and gives an oily platinochloride.

If the action of the water takes place at  $245^{\circ}$ , substances are formed which appear to be the leuco-compounds of (2) and (3), *i.e.*, which contain more hydrogen. These are yellow or colourless, and have not yet been obtained in a state of absolute purity.

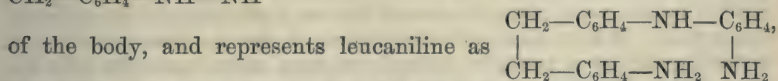
At  $270^{\circ}$ — $280^{\circ}$  yellow needles are formed, which appear to be the leuco-derivative of (4).

Together with these compounds, small quantities of phenol and of a tarry substance are produced, probably by secondary reactions; when dilute hydrochloric acid is used instead of water, little but toluidine and aniline is formed; when water acts on aniline or paratoluidine at  $240^{\circ}$ , no oxidised phenyl derivative is formed. Berthelot has shown that no phenol is thus formed from aniline at  $310^{\circ}$ .

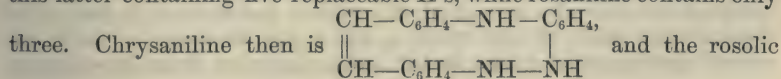
From these reactions the author infers the rosaniline formula



This is in harmony with the known reactions

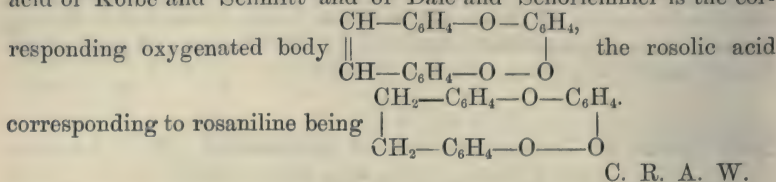


of the body, and represents leucaniline as this latter containing five replaceable  $\text{H}$ 's, while rosaniline contains only



three. Chrysaniline then is  $\begin{array}{c} || \\ \text{CH}-\text{C}_6\text{H}_4-\text{NH}-\text{NH} \end{array}$  and the rosolic

acid of Kolbe and Schmitt and of Dale and Schorlemmer is the corresponding oxygenated body



corresponding to rosaniline being

C. R. A. W.

**Researches on the formation of Aniline-red.** By ROSENSTIEHL (Dingl. polyt. J., cccii, 52—60, from Bulletin de la Société Industrielle de Mulhouse).

As the result of some careful and, for cotton printers, interesting experiments, the author states that—

Pseudo-toluidine when heated *by itself* with arsenic acid is partly converted into pseudo-rosaniline.

The same change takes place when pseudo-toluidine or one of its salts is exposed to the air.

This behaviour furnishes a most delicate colour reaction for pseudo-toluidine, and is not interfered with by the presence of toluidine or aniline.

The formation of pseudo-rosaniline occurs to a considerable extent in prints during the making of aniline-black, and is the cause of a disagreeable difficulty.

By the dry distillation of indigo with an alkali, a mixture of aniline and pseudo-toluidine is obtained.

C. H. G.

**Oxidation-products of the Methyl- and Ethyl-Phosphines.** By A. W. HOFMANN (Deut. Chem. Ges. Ber., v, 104—112).

In the course of recent researches (see this Journal) on the phosphines, undertaken by the author, the determination of the phosphorus in these bodies was attempted by heating with nitric acid in a sealed tube, with a view to subsequent precipitation by a magnesium salt. It was found, however, that the complete conversion of the phosphorus into phosphoric acid was possible only when operating with the strongest fuming nitric acid, and at very high temperatures.

The observation of this remarkable resistance to oxidation led to further experiments, from which it was found that, by treating the primary and secondary phosphines with nitric acid, new acids of great stability and only slight volatility are obtained.

*Monomethylphosphinic acid* is formed by passing methylphosphine gas, evolved on treating with water the crude product of the action of methyl iodide upon phosphonium iodide and zinc oxide, into fuming nitric acid. A little phosphoretted hydrogen being present in the gas, a small quantity of phosphoric acid is formed simultaneously with the new acid. In order to purify the latter the nitric acid solution is evaporated on a water-bath, and the residue is dissolved in water and treated with oxide of lead, which gives a salt insoluble in water but soluble in acetic acid. The acetic solution filtered from the insoluble



phosphate, and freed from lead by sulphuretted hydrogen, leaves on evaporation an oily liquid, which solidifies on cooling to a white spermaceti-like mass. The substance is easily soluble in water, reddens litmus paper, and possesses an agreeable acid taste. It also dissolves in alcohol and, to a smaller extent, in ether.

The stability of this compound is remarkable, for not only has fuming nitric acid no action upon it, but it may even be evaporated with aqua-regia without suffering the smallest change. It melts at  $105^{\circ}$ , and is volatile in great part without decomposition. Analysis indicates that the methyl-phosphine, by treatment with nitric acid, has fixed three atoms of oxygen, and the new compound has the formula  $(\text{CH}_3)_2\text{H}_2\text{PO}_3$ .

It is a well characterised acid, forming two classes of salts,  $(\text{CH}_3)_2\text{HM}'\text{PO}_3$  and  $(\text{CH}_3)_2\text{M}'_2\text{PO}_3$ .

The mono-metallic salts have an acid reaction, the dimetallic are alkaline.

The salts of the alkali-metals are soluble, and only slightly crystalline; the ammonium salt loses ammonia by evaporation, and leaves the acid. Many of the metallic salts are insoluble, or soluble with difficulty.

The primary silver salt,  $(\text{CH}_3)_2\text{HAgPO}_3$ , crystallises in white needles, which are easily resolved by water, and even by alcohol, into free acid and secondary salt  $(\text{CH}_3)_2\text{Ag}_2\text{PO}_3$ . The latter is a white, nearly insoluble powder. The primary lead salt is also decomposed by water. The secondary lead salt,  $(\text{CH}_3)_2\text{Pb}_2\text{P}_2\text{O}_6$ , is easily obtained pure as a white precipitate, almost insoluble in water, but soluble in acetic acid.

The barium salt is obtained in white microscopic needles by adding alcohol to the concentrated aqueous solution, or by slow evaporation as a gummy mass. Analysis showed this compound to be the primary salt,  $(\text{CH}_3)_2\text{H}_2\text{BaP}_2\text{O}_6$ .

Methylphosphinic acid has the same composition as methyl phosphorous acid, but is evidently totally different in properties from that body, which is uncrystallisable, and decomposable by a gentle heat into phosphorous acid and methyl alcohol.

*Dimethyl-phosphinic Acid.*—This compound results from the action of nitric acid on the secondary methyl-base.

Dimethyl-phosphine is obtained when the crude product of the action of phosphonium iodide on methyl iodide, after expulsion of the methyl-phosphine by water, is distilled with an alkali. A solution of this body in hydrochloric acid was mixed with fuming nitric acid, and after the reaction was over, the liquid was evaporated, saturated with silver oxide, and the solution of the silver salt treated with sulphuretted hydrogen. The solution of the acid thus obtained gave on evaporation a white crystalline mass, becoming slightly brown in the air. The new compound is very soluble in water, alcohol, and ether, and the solutions have an acid reaction. The crystals melt at  $76^{\circ}$ , volatilise without decomposition at a higher temperature, and the distilled product exhibits an unchanged melting point. This acid being less suited for analysis than the monomethyl-compound, the formula was ascertained by an analysis of the silver salt. From this it was found that the dimethyl-phosphine, by treatment with nitric acid, had

fixed two atoms of oxygen, and that the formula of the new acid must be  $(\text{CH}_3)_2\text{HPO}_2$ . It, therefore, forms only one series of salts.

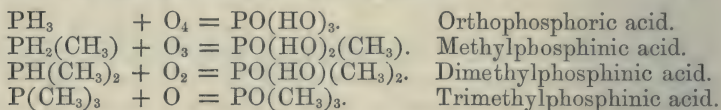
The silver salt,  $(\text{CH}_3)_2\text{AgPO}_2$ , was obtained in white needles, extraordinarily soluble in water, but very slightly soluble in absolute alcohol and ether. The barium and lead salts are neutral, very soluble uncrystallisable compounds.

Experiments in the ethyl series have demonstrated the existence of two ethylated acids corresponding to those just described.

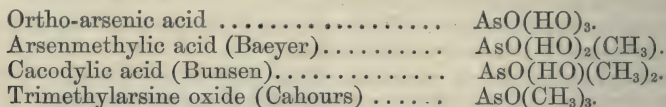
*Ethyl-phosphinic acid* agrees with the methyl compound in mode of preparation, appearance, and properties. It melts at  $44^\circ$ . The formula  $(\text{C}_2\text{H}_5)_2\text{H}_2\text{PO}_3$  was deduced from the analysis of the silver salt, which is an amorphous yellowish powder, insoluble in water and alcohol.

*Diethylphosphinic acid* has not been obtained in the crystalline state, but only as a liquid which did not solidify even at a temperature of  $-25^\circ$ . The silver salt, however, is crystalline, and is represented by the formula  $(\text{C}_2\text{H}_5)_2\text{AgPO}_2$ .

The existence and composition of the acids thus established serve to connect together orthophosphoric acid, and the oxides of the tertiary phosphines discovered years ago by the author in conjunction with Cahours. The relationship which subsists between these bodies is illustrated by the following series of equations:—



This group, however, does not stand alone. A similarly symmetrical series finds a starting point in ortho-arsenic acid. Its members, however, are not at present producible in the same manner as the corresponding bodies containing phosphorus, inasmuch as the primary and secondary arsines, by the oxidation of which they would be produced, are at present unknown.



W. A. T.

**Aromatic Phosphines.** By A. W. HOFMANN (Deut. Chem. Ges. Ber., v, 100—104).

EXPERIMENTS made for the purpose of obtaining phosphines corresponding with aniline and toluidine, failed; but the benzyl-phosphines are readily formed by heating crude benzyl chloride with phosphonium iodide and zinc oxide. On distilling the product with steam, a heavy oil passes over, being a mixture of regenerated toluene and of benzylphosphine, which are separated by fractional distillation. Benzylphosphine,  $\left. \begin{matrix} \text{C}_7\text{H}_7 \\ \text{H}_2 \end{matrix} \right\} \text{P}$ , boils at  $180^\circ$ ; in contact with the air it takes up oxygen

with rapidity, thick white fumes being formed, and the temperature rising  $100^{\circ}$  and more. Like other primary phosphines, it forms a crystallised hydriodide, which is decomposed by water. The hydrobromide and hydrochloride do not crystallise; the latter gives yellow a with precipitate platinum chloride.

Dibenzylphosphine,  $\left. \begin{matrix} (C_6H_5)_2 \\ H \end{matrix} \right\} P$ , is formed, together with the primary base, and remains behind on distillation. It crystallises from alcohol in large odourless and tasteless needles, which are grouped in stars or fascicles; they melt at  $205^{\circ}$ , and volatilise at a higher temperature with partial decomposition. It is insoluble in all acids, differing in this respect from the secondary ethyl- and methyl-phosphines, which are basic compounds, but resembling the secondary aromatic amines, which do not readily combine with acids. Dibenzylphosphine is stable in the air, even at a higher temperature.

C. S.

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**Researches on the Uric Acid Group. (No. II.)** By M. NENCKI  
(Deut. Chem. Ges. Ber., v, 45).

THE product obtained on heating sulphopseudo-uric acid with concentrated sulphuric acid to  $200^{\circ}$ , previously described in this Journal (ix, 1058), has been further examined. The greatest yield is obtained when the temperature is not allowed to exceed  $160^{\circ}$ ; under these circumstances but little sulphurous anhydride is evolved, which proves to be the product of a secondary reaction. The numbers obtained on analysis correspond better with the formula,  $N_4C_5SO_2H_4$ , than with that previously assigned to the compound, so that the action of sulphuric acid consists simply in withdrawing the elements of water from sulphopseudouric acid.

The yield of the new body—*urosulphinic acid*—is far less if the heating with sulphuric acid is continued; much sulphurous anhydride is then evolved, and, on evaporating the acid solution, it furnishes a new compound also containing sulphur.

Urosulphinic acid is intermediate in chemical behaviour between uric acid and xanthine; it is a weak monobasic acid, being precipitated from an alkaline solution by carbonic acid.

All attempts to withdraw sulphur from it were unsuccessful, and it would appear that it is impossible to effect this without entirely destroying the molecule.

H. E. A.

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**Parabanic Acid.** By B. TOLLENS (Zeitschr. f. Chem. [2], viii, 533).

IF urea could be combined with cyanogen, and in the compound thus formed  $2CN$  could be converted into  $2CO$  by means of dilute sulphuric acid, parabanic acid would be formed; but experiments made to effect this synthesis gave only negative results.

C. S.



**A Chromo-glucoside, from the Seed of *Melampyrum arvense*.**

By H. LUDWIG and H. MÜLLER (Arch. Pharm. [2], xlix, 6—10).

*Melampyrum arvense* frequently grows in Germany amongst the corn; the seed, which is similar in appearance to wheat, communicates a reddish-violet colour to the bread containing it. By exhausting the seeds with alcohol, removing fat from the extract, and allowing the purified alcoholic solution to evaporate over oil of vitriol, about 1 per cent. of a reddish-brown substance, crystallised in needles, is obtained; by a second crystallisation the body is obtained white. Boiled with an acid, this colourless body splits up into glucose, and an insoluble substance of a violet-brown colour. The authors describe numerous reactions of the glucoside in question, and conclude that it is identical with, or at least remarkably similar to rhinanthin, a substance they have already described (Arch. Pharm. [2], cxlii, 203) as obtained from *Rhinanthus alectorolophus*.

R. W.

**The Chromogen of *Boletus cyanescens* and other Fungi that become Blue after fresh Fracture.** By H. LUDWIG (Arch. Pharm. [2], cxlix, 107—117).

371 grams of *Boletus cyanescens* in shreds were digested with 500 c.c. of 92 per cent. alcohol, whereby an extract was obtained which, after filtration, was brownish-yellow, and then green, but gave an intense indigo-blue colour with sodium hypochlorite; after concentration, crystals of mannite were obtained from this extract; the mother-liquor, treated with alcohol and ether, yielded a golden-yellow solution, which left on evaporation a residue becoming deep green-brown with sodium hypochlorite.

The aqueous solution of the chromogen has a strong acid reaction; hydrochloric acid does not change its brownish-yellow tint; neither does soda-ley added to alkaline reaction; the latter, however, prevents the blue coloration with sodium hypochlorite from appearing. The chromogen contains nitrogen, as, on heating with caustic potash, ammoniacal vapours are given off; cyanides are absent, and aniline could not be found after addition of soda-solution to alkaline reaction, extraction with ether, addition of hydrochloric acid to the ethereal extract, evaporation, and testing of the residue with a little soda solution and sodium hypochlorite (Phipson concluded on very slender evidence that both *Boletus cyanescens* and *B. luridus* contain aniline).

Dr. Gonnermann has also found the same reaction with sodium hypochlorite with the chromogens similarly extracted from *B. luridus*, *B. rufus*, *B. Satanas*, *B. pachypus*, *B. Calopus*, and the brown-tubed variety of *B. variegatus*; and is about to pursue further researches conjointly with the author.

C. R. A. W.

## PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XII.—*The Chemistry of the Hydrocarbons.*

[A Lecture delivered before the Chemical Society, April 4th, 1872.]

By C. SCHORLEMMER, F.R.S.

It is now nearly 200 years since Lemery, in his celebrated "*Cours de Chymie*," separated mineral bodies from vegetable and animal substances, and since that time chemistry has been divided into organic and inorganic chemistry. Such a division appeared quite natural at a time when chemistry formed only a part of descriptive natural science; yet even at that period the founders of the phlogiston-theory considered it unscientific to divide chemical substances according to their origin, and they endeavoured to justify such a classification from a chemical point of view. Thus Becher says, "The elements occurring in the three natural kingdoms are the same, but they are combined in mineral bodies in a manner more simple than they are in vegetable and animal substances." Stahl thought that in minerals the earthy principle preponderated whilst organic bodies contained more phlogiston and more of the aqueous principle. If we translate these definitions into our present chemical language, we find that they are identical with views which were held not long ago.

When, with the discovery of oxygen, the era of quantitative chemistry commenced, the distinction between organic and inorganic bodies was still kept up, because it was observed that compounds formed by the vital process possess certain peculiarities by which they can be easily distinguished from mineral substances.

"Whilst formerly," as Kekulé says, "chemistry was divided because a boundary was seen; afterwards such a boundary was looked for, because it was found convenient to have one" (*Kekulé's Lehrbuch*, I, 8). This appeared easy enough at first; chemists then understood both how to decompose mineral compounds into their constituent elements, and also how to build them up again.

But such was not the case with organic bodies; their composition could be easily ascertained, but all efforts made to effect the synthesis of such compounds failed; and hence Berzelius assumed that "the elements present in living bodies obeyed laws totally different from those which rule inanimate nature." It was said that organic bodies might be changed by chemical processes into other organic compounds,

but it was thought to be impossible to obtain any such body by synthesis.

The further development of chemistry soon showed that these views were erroneous. As soon as a clear insight into the chemical constitution of organic bodies was gained, methods were found by means of which bodies hitherto formed only by the vital process could be built up from their elements.

Now when the fact was established that the same chemical laws rule alike animate and inanimate nature, the difficulty presented itself of fixing a boundary line by which inorganic bodies might be separated from organic compounds. I need not dwell here upon all the views brought forward to explain the difference between these two divisions. You all know how the definitions of organic chemistry were changed from year to year, until in 1848 Gmelin first called attention to the fact that carbon was the only element essential to organic compounds. He said, "If we regard as organic those carbon-compounds which have hitherto been classed among inorganic substances, viz., carbonic oxide, carbonic acid, sulphide of carbon, phosgene, cast-iron, &c., we might define organic compounds simply as the compounds of carbon. But the organic compounds are still further distinguished by containing more than one atom of carbon. Hence the term *organic compounds* includes all primary compounds containing more than one atom of carbon" (*Gmelin's Handbook*, vii, 5).

At that time the true atomic weight of carbon was not known, and thus the above compounds were separated from organic substances, whilst methyl and formyl compounds were included amongst them. As soon as the true atomic weight of carbon was established, Gmelin's definition fell to the ground. It was then said, that organic chemistry was simply the chemistry of the carbon-compounds. Kekulé, who first distinctly advocated this view says (*Lehrbuch* 1), "There is no natural boundary line between organic and inorganic chemistry, and if we still retain this division, it is only as a matter of convenience. We treat the carbon-compounds separately on account of their large number and their importance."

Erlenmeyer expresses similar views; he thinks (*Lehrbuch d. Org. Chem.*, 5) "that a division of labour is requisite in the interest of teaching." "Besides," he adds, "it cannot be denied that by reason of certain properties possessed by carbon, the carbon-compounds exhibit several peculiarities in their chemical behaviour, so that their study requires in many respects other methods of investigation than those employed in the study of the compounds of the other elements, and thus the necessity for a division of labour has also made itself apparent in the interests of scientific research."

Butlerow also says (*Lehrb. d. Org. Chem.* 5), "organic chemistry



must now be defined as the chemistry of the carbon-compounds. If such a definition is somewhat unnatural and not exactly correct, it is still very convenient." I think, however, that such a division is more than a mere matter of convenience. The compounds of carbon do really differ from those of the other elements, because carbon itself exhibits certain properties which no other element possesses.

Kekulé, who first showed that carbon is a tetrad element, pointed out at the same time that the existence of such an immense number of carbon-compounds can be easily explained by assuming that the atoms of this element have the property of combining with each other. The same view was expressed by Couper.

This property is also possessed by other polygenic elements as sulphur and oxygen, but whilst in the case of the latter elements the number of atoms uniting together in this way is very limited, we have not yet found such a limit to exist in the case of carbon.

*It is, therefore, most characteristic for tetrad carbon, that a large number of its atoms can be linked together to form a group, which in a great many reactions remain together, and act like a single atom.*

But carbon possesses yet another property in common with no other element. *All the combining units in such a group, which are not saturated with carbon, can be saturated with hydrogen.*

Thus whilst most of the metals do not combine with hydrogen at all, and the other elements form only one or two, or at the most three compounds with hydrogen, we find not only that very many hydrocarbons exist, but that their number is daily increased by the discovery of new ones.

The hydrocarbons are not only the most simple of the carbon-compounds, but from a theoretical point of view also the most important, because all other carbon compounds can be regarded as derivatives of them, or as being formed by substitution of other elements for hydrogen. This is shown by the fact that a considerable number of vegetable and animal substances can be prepared artificially from hydrocarbons. On the other hand, as soon as the constitution of a carbon-compound is understood, we are in a position to convert it into the hydrocarbon from which it has been theoretically derived.

In the majority of carbon-compounds occurring in nature, a portion of the hydrogen of the original hydrocarbon is replaced by oxygen, and in others by nitrogen; all the other elements can, however, be introduced artificially into carbon-compounds. But there are only a few cases in which all the hydrogen can be replaced.

Thus the number of carbon chlorides is much smaller than that of the hydrocarbons. With oxygen, carbon forms only two compounds, and with nitrogen it unites in only one proportion. From this it follows that the great majority of carbon-compounds contain hydro-

gen, that there is present in them a residue of the original hydrocarbon.

We may therefore define that part of our science, which is commonly called Organic Chemistry, as *the Chemistry of the Hydrocarbons and their derivatives*.

I now propose to lay before you, in a short sketch, how far our knowledge of the hydrocarbons has advanced.

*Paraffins*.—Kekulé first pointed out that, when two atoms of carbon combine, the most simple and therefore the most probable case is, that one combining unit of one atom enters into combination with one combining unit of the other atom. The group  $C_2$  thus formed is consequently a hexad. When more than two atoms of carbon are linked together, they may combine in a similar manner, one-fourth of the combining capacity of one atom being saturated by one-fourth of the combining capacity of another. By saturating the free combining capacities of such a group with hydrogen, we obtain a series of hydrocarbons, having the general formula,  $C_n H_{2n+2}$ , to which the name *paraffins* has been given. This name was originally applied to the solid members of the series, on account of their chemical indifference; but as the gaseous and liquid members exhibit the same character it appears convenient, as H. Watts has suggested, to employ the term paraffin as a generic term for the whole series.

The most characteristic property of the paraffins is that they are not capable of uniting with any other bodies, and for this reason they have also been called *saturated hydrocarbons*.

We are at present acquainted with a considerable number of paraffins, amongst which there are found many isomerides. To explain the isomerism in this series two assumptions have been made.

One which found many advocates up to the year 1864 was that the four combining units of the carbon atom have not the same value or the same function. This assumption was made in order to explain the existence of two isomeric hydrocarbons having the formula  $C_2H_6$ , it being believed at that time that methyl gas was different from ethylhydride. But Crum-Brown has shown that there is a certain degree of inconsistency in this hypothesis (*Trans. Roy. Soc. Edin.*, xxiii, 707). Butlerow, in endeavouring to explain the isomerism of these two hydrocarbons, argued that in methyl gas the two atoms of carbon were combined by two combining units of the same kind (which he called secondary affinities) each being the combining unit which in methyl iodide is saturated with iodine. In hydride of ethyl the carbon atoms are united in the same way as in other ethyl compounds, and therefore probably as in the acetyl compounds, one of which is acetonitrile or methyl cyanide; the one is therefore the com-

bining unit of methyl, and the other that of cyanogen. These must be different, because the two hydrocarbons are not identical. To indicate this, Butlerow calls the free combining unit of cyanogen a primary affinity. We have thus in methyl gas two secondary affinities united together, and in hydride of ethyl a primary united to a secondary. "But by carrying this argument a little further, we arrive," says Crum-Brown, "at an absurdity; thus the carbon radical of acetic acid is the same as that of oxyacetic acid, and that again is the same as the carbon radical of oxalic acid, and therefore as that of oxalic nitrile or cyanogen gas. In cyanogen gas, however, we have the two carbon atoms united by two primary affinities; but we have before proved that in the acetic acid series they are united by a primary affinity of the one to a secondary of the other. It is obvious, then, that at least one of our assumptions is false."

About at the same time I proved by experiment that methyl gas or dimethyl is identical with ethyl hydride; and since that time a few chemists only have made use of the above hypothesis in order to explain certain cases of isomerism.

If the four combining units of the carbon atom have the same value, isomerism in the paraffin series can only be caused by a different grouping of the carbon atoms; and in this case it is easy to find out the number of isomerides which can exist in the case of each member of the homologous series. According to this theory, the first three members are not susceptible of isomeric modifications, whilst the four-carbon paraffin,  $C_4H_{10}$ , can exist in two, and the five-carbon paraffin in three isomeric forms, &c.

This theory is completely borne out by facts. Of the three lowest members, no isomeric forms are known, but we are acquainted with two containing four atoms of carbon, and with three containing five atoms.

Some time ago I showed that all the paraffins of known structure may be divided into four groups:—

- (1.) Those in which each carbon atom is directly combined with at most two carbon atoms.
- (2.) Those in which one carbon atom is united directly with three others, or which contain the group isopropyl.
- (3.) Those containing the group isopropyl twice.
- (4.) Those in which one carbon atom is combined directly with four others.

Of these groups, the first, which I called normal paraffins, was at that time only imperfectly known. Indeed, the structure of some of the members was not proved at all: they were placed there only because it appeared for several reasons probable that they possessed a



very simple structure. Since that time, however, I have increased their number, and proved that the hydrocarbons placed in this group are really normal paraffins.

The only means we hitherto possessed for determining the constitution of a paraffin was either to obtain it from an alcohol or other compound of known structure, or to convert the paraffin into an alcohol, and then endeavour to find out the constitution of the latter.

The latter method, however, has been surrounded by such difficulties, that it appeared almost impossible to make use of it. I have, however succeeded in overcoming some of those obstacles and been able to obtain much larger quantities of the alcohols than formerly, so that I could study fully their products of oxidation. An investigation of the paraffins contained in Pennsylvanian petroleum showed that they belong to the first group, as the alcohols derived from them, as well as the acids obtained by oxidising the latter, were found to be normal compounds.

Before I take leave of the paraffins, I have to say a few words about the paraffins *par excellence*, viz., the solid paraffins. These bodies, which resist so energetically the action of chemical agents that they have obtained their name from this fact, appear to be very unstable bodies at a high temperature, although, curiously enough, they are produced by destructive distillation. Thorpe and Young have shown (*Proceedings of the Royal Society*, xix, 370), that by distilling solid paraffin under pressure, it is almost completely resolved, with evolution of but little gas, into hydrocarbons which remain liquid at the ordinary temperature, and consist principally of olefines.

*Olefines*.—By abstracting two atoms of hydrogen from the paraffins we obtain the second group of hydrocarbons, called by Guthrie the olefines.

These olefines exhibit in their physical properties, as specific gravity, boiling points, &c., great resemblance to the corresponding members of the paraffin series. They are, however, easily distinguished from the latter by the fact that they combine with great energy with the elements of the chlorine group, for which reason they have also been called non-saturated hydrocarbons.

To account for their constitution there exist three hypotheses:—

- (1.) They contain carbon atoms with free combining units.
- (2.) One of the carbon atoms is no longer a tetrad, but a dyad.
- (3.) One carbon atom is linked with two combining units to two combining units of another.

The first hypothesis found many adherents some years ago. Amongst these Lothar Meyer has very clearly stated the reasons why the hypothesis that the so-called non-saturated compounds contained free

combining units was much more probable than the view adopted by Kekulé, that a double linking of carbon atoms occurred in them. He says (*Ann. Chem. Pharm.*, cxxxix, 285) "that in the first place this hypothesis offers no philosophical difficulty; that it cannot be astonishing that under certain conditions one or more affinities remain unsaturated; on the contrary, it would be wonderful if such non-saturated affinities did not exist."

"For certain compounds this theory is even unavoidable, as for nitric oxide, carbonic oxide, the vapour of mercury, cadmium, &c."

Now according to this theory the most simple olefine known, ethylene,  $C_2H_4$ , ought to exist in two isomeric forms, viz. :—

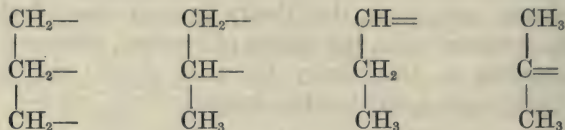


However, experiments made by Meyer and by Tollens for the purpose of obtaining an isomeride of ethylene failed. But although the two isomeric modifications of ethylene have not been obtained, yet it was stated that two different chlorine-substitution products of ethylene exist, viz., *monochlorethylene* or *vinyl chloride*, obtained by Regnault, and *chloracetene*, which Harnitz-Harnitzky prepared by the action of phosgene upon aldehyde. As both compounds had been repeatedly investigated by other chemists, their existence could hardly be doubted, and could only be explained either by assuming free affinities or by the theory of dyad carbon. The existence of a compound isomeric with chlorethylene is certainly of the highest importance to the theory, because, as Kekulé has pointed out, if the existence of dyad carbon is proved in such a simple case, the same assumption is at least admissible in more complicated cases. Kekulé in conjunction with Zincke therefore repeated Harnitzky's experiments (*Ann. Chem. Pharm.*, clxii, 125). They said that from their theoretical stand-point, the existence of chloracetene not only appeared improbable, but that the properties ascribed to this body, as well as the reaction by which it was formed, were so remarkable that it appeared necessary to make the personal acquaintance of chloracetene. Although it appeared improbable that this body was really isomeric with Regnault's vinyl chloride, yet it might be a polymeride, which by dissociation yields a lighter vapour. It was also possible that vinyl chloride had not been obtained in a pure state, and was identical with chloracetene, and there was also the probability that all the statements about this latter compound were erroneous. The result of this investigation was that the last view was the correct one. They found that the most remarkable property of this remarkable compound was its non-existence.

According to the theory of dyad carbon, only one ethylene can

exist having the constitution  $\text{CH}_3 - \text{CH}$ . But that the known ethylene has not this constitution is proved by the fact that its chlorhydrin yields by oxidation monochloracetic acid (*Zeitschr. f. Chem.* [2], vii, 263).

Another proof against the existence of free combining units, or of dyad carbon, is found in the fact that only one propylene is known, of which hydrocarbon four modifications ought to exist, according to the theory of free combining units, viz. :—



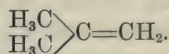
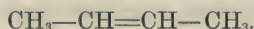
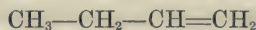
or only the latter two in the case of the dyad carbon theory.

Friedel and Ladenburg, as well as Butlerow, failed to obtain an isomeride of common propylene. The two former chemists tried to obtain the last of the four forms, by acting with sodium upon the so-called methyl-chloracetol,  $\text{CH}_3 - \text{CCl}_2 - \text{CH}_3$ , but obtained, instead of it, only the well known propylene, which was formed by a molecular change taking place.

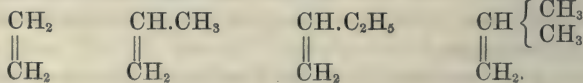
From these, and other examples, we must conclude that the olefines contain neither dyad carbon nor free combining units, and that they are really saturated compounds, containing two carbon atoms linked together by two combining units of each.

Butlerow has some time ago added a fresh proof of the correctness of this hypothesis; of this I shall have to speak when I come to the next group.

The number of isomeric olefines capable of existing is larger than that of the corresponding paraffins, as the double linking of the carbon atoms can take place in different parts of the hydrocarbon. Thus there exist only two butanes, but three butylenes, viz. :—

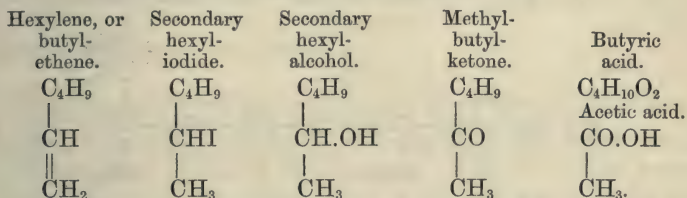


The number of isomerides known is, however, not large at present; nearly all those which have been better investigated contain the two carbon atoms, which are linked together by two combining units situated at the end of the chain. These may therefore be considered as being derived from ethylene by the substitution of a monad alcohol-radical for one atom of hydrogen, thus :—

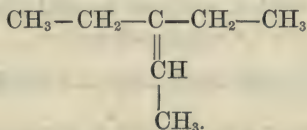




The constitution of these olefines has been fully proved by experiment. On combining them with hydriodic acid, secondary iodides are formed, which, when converted into alcohols, yield acetones, containing the group methyl, as on oxidation they yield acetic acid, besides another fatty acid. Now Popoff has established the law that when an acetone is oxidised, the more simple alcohol-radical always remains combined with the group carbonyl, whilst the other is oxidised by itself, yielding a fatty acid containing the same number of carbon atoms as the alcohol radical itself (*Ann. Chem. Pharm.*, cxlv, 283, and clxi, 285). Thus when hexylene, obtained from mannite, is subjected to the above reactions, we obtain acetic acid and butyric acid :—

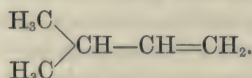


Besides these olefines, Butlerow has lately described some in which carbon atoms situated in the middle of the chain are linked together by two units. The constitution of these bodies, which were obtained from tertiary compounds, is easily understood, as the constitution of the alcohols from which they have been derived is well known. Thus, on acting with alcoholic potash on the iodide of triethyl-carbinol,  $CI(C_2H_5)_3$ , a pseudoheptylene is obtained, having the following constitution :—

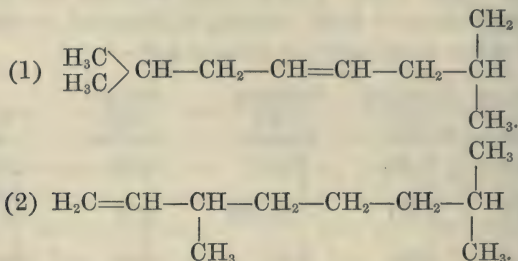


Besides the olefines which are derived from compounds having the general formula  $C_nH_{2n+1}R$  ( $R$  representing a monad radical), by the abstraction of  $HR$ , there exists another group, formed by the polymerisation of the members of the first group. Of these poly-olenes, as Schneider calls them, only one, diamylene, has been more closely studied by this chemist (*Ann. Chem. Pharm.*, clvii, 185). This hydrocarbon, which is most readily formed by shaking amylene together with cold dilute sulphuric acid, yields, as the first product of oxidation, diamylene oxide, which by further oxidation splits up, with formation of carbon dioxide, acetic acid, and amethenic acid,  $C_7H_{14}O_2$ , a peculiar compound which is isomeric with cœnanthylic acid, from which however it differs by exhibiting only very feeble acid properties.

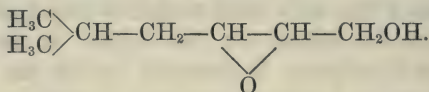
Erlenmeyer has shown that amylene has the following constitution:—



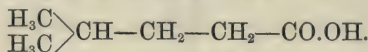
Now as diamylene combines as easily with bromine as amylene does, it would appear as most probable that in the former compound two carbon atoms are combined in the same manner as in other olefines, thus:—



But if either of these two formulæ expressed its constitution, two atoms of hydrogen would have to change places during its formation from amylene. This, however, appears improbable, as diamylene is so easily formed in the cold. By assuming the first formula as correct, the constitution of amethenic acid would be—

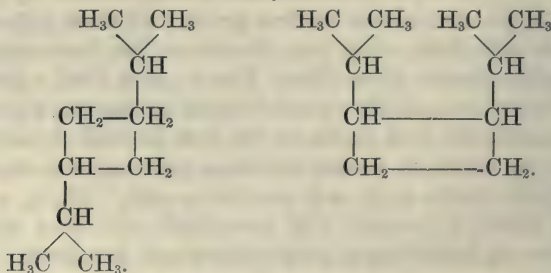


which represents an alcohol, and not an acid. Accepting the second formula, we should have for amethenic acid—

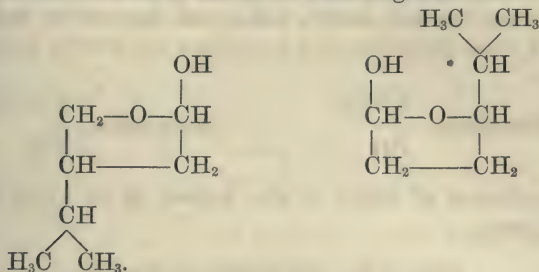


which would be a strong acid, because it contains the group carboxyl, and, moreover, no acetic acid could be formed at the same time.

It appears, therefore, most probable that one of the following formulæ represents the constitution of diamylene.



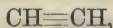
The acid would then have one of the following formulæ:—



Both explain equally well why this singular compound is so weak an acid, as both contain the group  $\begin{array}{c} \text{HC—O} \\ | \\ \text{CH} \end{array}$  or carboxyl in which half an oxygen atom is replaced by hydrogen.

*Hydrocarbons of the Acetylene Series.*—By again abstracting from the olefines two other atoms of hydrogen, we obtain the third group of hydrocarbons, of which acetylene,  $\text{C}_2\text{H}_2$ , is the first member. This body is remarkable as being the only hydrocarbon which has been obtained by the direct union of its elements.

A general method of obtaining the hydrocarbons of this series is to abstract two molecules of hydrobromic acid from the bibromides of the olefines. As this mode of formation is quite analogous to that by which paraffins are converted into olefines, it appears most probable that the acetylene-hydrocarbons have a constitution similar to that of the olefines. In acetylene the two carbon atoms are linked together by three combining units of each atom—



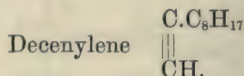
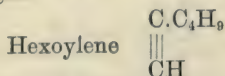
and its homologues contain a monad alcohol-radical in place of one atom of hydrogen.

I have already mentioned that Butlerow has made some experiments for the purpose of proving the correctness of the theory which assumes that the non-saturated hydrocarbons contain carbon-atoms linked together by more than one unit of their combining capacity (*Journ. Chem. Soc.* [2], ix, 214). According to him, isobutylene,  $(\text{CH}_3)_2\text{C}=\text{CH}_2$ , could not, by the loss of two atoms of hydrogen, yield crotonylene,  $\text{C}_4\text{H}_6$ , but an isomeride with a closed group of three carbon atoms.

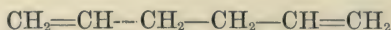
He found, however, that by the action of sodium ethylate upon monobrom-isobutylene,  $(\text{CH}_3)_2\text{C}=\text{CHBr}$ , no hydrocarbon is formed, but ethyl-isocrotyl ether,  $\left. \begin{array}{c} \text{C}_2\text{H}_5 \\ \text{C}_4\text{H}_6 \end{array} \right\} \text{O}$ . Instead of hydrobromic acid being taken out, bromine was replaced by oxethyl.



The number of isomeric hydrocarbons in this series is very small. They are hexoylene and diallyl,  $C_6H_{10}$ , and decenylenes and rutylenes,  $C_{10}H_{18}$ . Of these hexoylene and decenylenes are strictly homologous to acetylene—



The constitution of diallyl is also known, as we know that of the allyl compounds—



Rutylenes have been obtained from diamylenes, its constitution is, therefore, probably similar to that of the latter hydrocarbon, which has already been fully discussed.

*Hydrocarbons of the Series  $C_nH_{2n-4}$ .*—Of this group only two have been artificially prepared, by abstracting hydrogen from the corresponding members of the preceding series. One of these, valylene,  $C_5H_6$ , has been studied very little, the other,  $C_{10}H_{16}$ , which has been obtained from rutylenes, is isomeric with a large number of hydrocarbons, called the terpenes, existing in plants, chiefly in coniferæ and citrus species.

I need not here dwell upon the peculiar properties of this remarkable group of isomerides; I wish only to point out what we know of their chemical constitution, on which just lately a little light has been thrown.

All terpenes possess the property of being easily converted by several chemical agents into new isomeric modifications, and these may be changed again into new isomerides, but all yield at the end one and the same product, called *terebene*, the most characteristic property of which is, that it forms with hydrochloric acid a semi-hydrochloride,  $(C_{10}H_{16})HCl$ .

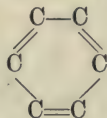
Now, according to Bauer and Verson (*Ann. Chem. Pharm.*, cli, 52), the hydrocarbon,  $C_{10}H_{16}$ , formed by heating rutylenes dibromide with an alcoholic solution of potash, exhibits all the characteristic properties of terebene, and appears to be identical with it. As the constitution of amylenes, from which rutylenes is derived, is known, we are in a position to draw some conclusions as to the constitution of terebene, of which I have to say more further on.

On oxidising terpenes, terephthalic acid is always formed, amongst other products. This compound is also a product of oxidation of several hydrocarbons of the aromatic group. This fact points out that the terpenes must be nearly related to the aromatic hydrocarbons, and this has been quite recently fully proved by Oppenheim, who has

shown that, by abstracting two molecules of hydrobromic acid from the dibromide of turpentine, cymene is formed.

*Aromatic Hydrocarbons.*—These hydrocarbons, as well as their derivatives, have been very fully investigated during the last few years. We owe to Kekulé our present theory of the aromatic compounds; he first called attention to the following points:—

1. All aromatic compounds contain a common nucleus, consisting of six atoms of carbon.
2. These six atoms are linked together in such a way that six combining units remain unsaturated.
3. All aromatic compounds are formed by saturating these free units with other elements or radicals.
4. The differences observed in certain groups of isomeric aromatic compounds are caused by the different relative position of certain elements or radicals in the nucleus.
5. The carbon-atoms forming the aromatic nucleus are united together by one and two combining units alternately.



Although several chemists have proposed certain modifications of this hypothesis, all the facts with which we are as yet acquainted prove that Kekulé's view is the most simple and most probable.

The most simple aromatic hydrocarbon is benzene,  $C_6H_6$ ; its homologues are derived from it by substitution of monad alcohol-radicals for hydrogen. The number of isomerides amongst these hydrocarbons is very considerable. Thus the hydrocarbon  $C_8H_{10}$  exists in four different modifications, viz., ethyl-benzene,  $C_6H_5.C_2H_5$ , and three different dimethyl-benzenes,  $C_6H_4 \begin{cases} CH_3 \\ CH_3 \end{cases}$ , the isomerism of the latter being caused by the different position of the two methyl-groups.

By representing benzene as a hexagon, and numbering the six corners, where the carbon-atoms are supposed to be, we can easily see the possibility of the existence of three dimethyl-benzenes—



The positions of the methyl groups being—

$$1 : 2; \quad 1 : 3; \quad 1 : 4.$$

No further different positions of the methyl groups are possible, for  $1 : 5 = 1 : 3$ , and  $1 : 6 = 1 : 2$ .

As the isomeric aromatic hydrocarbons have generally a great resemblance in their physical properties, it is of the highest importance to have means for distinguishing them from each other. This can be done by studying their products of oxidation.

When an aromatic hydrocarbon is heated with very dilute nitric acid, one of the alcohol radicals is oxidised to carboxyl. Methyl-benzene, ethyl-benzene, amyl-benzene, and all other hydrocarbons containing only one alcohol-radical yield one and the same product, viz., benzoic acid,  $C_6H_5.CO.OH$ . The formation of this acid proves, therefore, the existence of only one alcohol-radical in a hydrocarbon. The three methyl-benzenes, as well as methyl-ethyl benzene, yield isomeric methyl-benzoic acids,  $C_6H_4 \begin{Bmatrix} CH_3 \\ CO.OH \end{Bmatrix}$ , whilst diethyl benzene gives ethyl-benzoic acid.

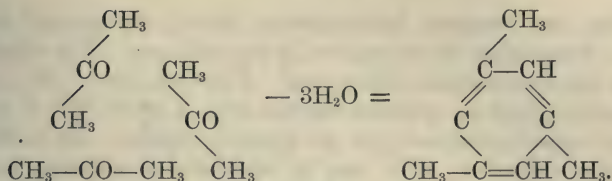
By acting on the hydrocarbons or their first oxidation products with stronger oxidising agents, such as dilute chromic acid, every alcohol-radical is oxidised to carboxyl, the three dimethyl-benzenes, as well as methyl-ethyl benzene and diethyl-benzene, yielding bibasic acids, having the composition  $C_6H_4 \begin{Bmatrix} CO.OH \\ CO.OH \end{Bmatrix}$ , &c.

But we are not only able to fix the number of alcohol radicals present in an aromatic hydrocarbon, but we can also determine their relative positions. Thus we know that in these dimethyl-benzenes the positions of the methyl-groups are—

Orthoxylene.	Isoxylene.	Methyltoluene.
1 : 2.	1 : 3.	1 : 4.

This has been proved in the following way. Three bibasic acids are known, having the composition  $C_6H_4 \begin{Bmatrix} CO.OH \\ CO.OH \end{Bmatrix}$  known, viz., phthalic acid, isophthalic acid, and terephthalic acid. In phthalic acid the two carboxyls occupy the position 1 : 2; this we see from the fact that this acid is produced by oxidising naphthalene, a hydrocarbon in which, as will be shown further on, two atoms of carbon are linked to two adjoining carbon-atoms of the aromatic nucleus. Isophthalic acid has been obtained by oxidising isoxylene, and isoxylene has been derived from mesitylene,  $C_6H_3(CH_3)_3$  a trimethyl-benzene in which, as Baeyer first pointed out, the three methyl groups have the symmetrical position 1 : 3 : 5. This follows from the mode of formation of this hydrocarbon, which is obtained by heating acetone with sulphuric acid. Three molecules of acetone lose three molecules of water, and the residues join together as follows:—





By oxidising mesitylene with weak nitric acid, we obtain monobasic mesitylenic acid,  $\text{C}_6\text{H}_3\left\{\begin{array}{l} \text{CH}_3 \\ \text{CO.OH} \\ \text{CH}_3 \end{array}\right.$ , which, when heated with lime, splits up into isoxylene and carbon dioxide. From this it follows that in isoxylene as well as in isophthalic acid, the two radicals occupy the positions 1 : 3 (or, which is the same, 1 : 5 or 3 : 5). As we now know, the constitution of phthalic acid and isophthalic acid, we know also that of terephthalic acid, in which the two carboxyl groups must be in the positions 1 : 4; and the two methyl groups in methyl-toluene are in the same position, because it yields terephthalic acid on oxidation. Hence in the only remaining dimethyl-benzene, viz., orthotoluene, the methyl groups must occupy the only other remaining positions 1 : 2. Thus, although the direct proof of the oxidation of this hydrocarbon to phthalic acid is wanting, because this acid is easily further oxidised by chromic acid, we still are able to arrive at a conclusion respecting its constitution.

To illustrate by an example how we can ascertain the constitution of an aromatic hydrocarbon by means of the above facts, I choose the following. There exist three isomerides having the formula  $\text{C}_{10}\text{H}_{14}$ , which on oxidation yield terephthalic acid, and consequently contain alcohol-radicals occupying the positions 1 : 4.

Of these three hydrocarbons two have been obtained by synthesis, viz., diethylbenzene and propyl-methyl-benzene; the third, called  $\alpha$ -cymene, occurs ready-formed in Roman cumin-oil, and in the oil from the water-hemlock, and has also been produced by the action of phosphorus pentasulphide upon camphor. Now as  $\alpha$ -cymene differs both from diethyl-benzene and propyl-methyl-benzene, it must be isopropylbenzene, no other isomeric form being possible. This view is confirmed by several facts. 1.  $\alpha$ -cymene boils at a lower temperature than propyl-methyl-benzene, and we always find that isopropyl compounds boil at a lower temperature than the corresponding normal-propyl compounds. 2. Isopropyl compounds readily yield propylene, and thymol, or the phenol of  $\alpha$ -cymene (*Journ. pract. Chem.*, [2], iii, 50) is easily decomposed into propylene and  $\gamma$ -cresol, by heating it with phosphorus pentoxide (*Zeitsch.*, 1869, 615). (3.) That  $\alpha$ -cymene contains isopropyl appears also probable from the analogy of cumene (*See Supplement of Watts's Dictionary*, 295 and 302).

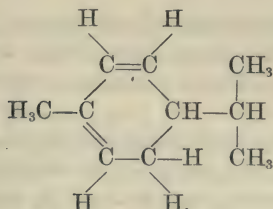
Besides the aromatic hydrocarbons having the general formula,  $C_nH_{2n-6}$ , there exists others containing less hydrogen. The constitution of these can also be readily ascertained. Thus styrolene,  $C_8H_8$ , obtained from styrax, yields on oxidation benzoic acid, a proof that it contains only one radical, combined with the aromatic nucleus. Its constitution is therefore  $C_6H_5.C_2H_3$ , or it may be considered as ethylene, in which one atom of hydrogen is replaced by the group,  $C_6H_5$ , and indeed in many of its reactions it behaves exactly like an olefine, combining with one molecule of bromine, &c., and being easily converted into polymeric modifications.

When styrolene dibromide is acted upon by alcoholic potash, two molecules of hydrobromic acid are abstracted from it, and acetenyl-benzene,  $C_6H_5.C_2H$ , is formed. This reaction corresponds exactly to the formation of acetylene from ethylene. Acetenyl-benzene shows, in fact, very great resemblance to acetylene, forming, like the latter, metallic derivatives, as  $C_6H_5.C_2Na$ ;  $C_6H_5.C_2Ag$ , &c.

Although the hydrocarbons which are homologous with benzene, behave in most of their reactions, like saturated hydrocarbons, yet, under certain conditions, they can be made to combine directly with other elements, like the olefines, and other so-called non-saturated compounds. Thus benzene can combine with one, two, and three molecules of chlorine. These chlorine addition-products still contain the carbon-atoms combined together in a closed chain; they are very unstable bodies, and are again readily converted into compounds in which the carbon atoms are linked together, as in benzene itself.

Also hydrogen can combine with aromatic hydrocarbons, but only with those which contain alcohol radicals. The number of the atoms of hydrogen combining with such a hydrocarbon, appears to depend, not only on the number of the radicals present, but also on their relative positions. Benzene does not take up hydrogen; methyl-benzene combines with one molecule, dimethyl-benzene (isoxylene) with two, and trimethyl-benzene (mesitylene) with three molecules.

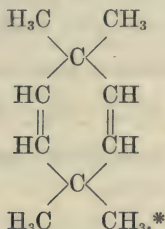
Oppenheim has shown (*Deut. Chem. Ges. Ber.*, v, 94) as I have already mentioned, that oil of turpentine belongs to these addition products. By abstracting two atoms of hydrogen from it, the hydrocarbon  $C_{10}H_{14}$  is formed, which must be either diethyl-benzene, or methyl-propyl-benzene, or  $\alpha$ -cymene, because oil of turpentine yields terephthalic acid on oxidation. It appears most probable that it is  $\alpha$ -cymene, as it has the same boiling point as the latter, and moreover oil of turpentine, as well as  $\alpha$ -cymene, occur ready-formed in plants. The constitution of oil of turpentine is therefore probably the following:—



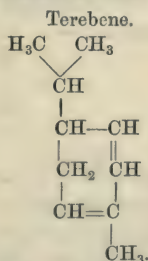
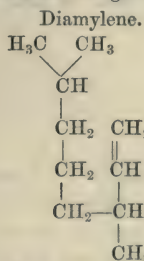
Oil of turpentine, therefore, contains the aromatic nucleus, in which the connection between two carbon atoms has been loosened, and thus two combining units, which in the aromatic nucleus were linked together, are now saturated with hydrogen. As Baeyer has shown, such a loosening of the connection between two carbon-atoms takes place most readily between those which are combined with alcohol radicals.

It has been already stated, that by abstracting four atoms of hydrogen from diamylene, a terpene is formed which seems to be identical with terebene. It has, however, not been yet shown whether this artificial terebene yields terephthalic acid on oxidation. If this is found to be the case, the constitution of this hydrocarbon would be as follows,

low, amylene being  $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH}-\text{CH}=\text{CH}_2 \\ \diagup \\ \text{CH}_3 \end{array}$ .



\* Since the above has been written, von Richter (*Deut. Chem. Ges. Ber.*, v, 334) has published a note on the condensation of diamylene to rutylen and terebene. He thinks that von Schneider's formula of diamylene does not explain either the property of this hydrocarbon of forming additive compounds, or its conversion into rutylen and terebene. He gives the following formulæ as much more probable:—



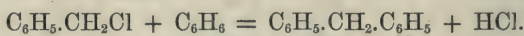
The formula of terebene is, as will be seen, the same as that which Oppenheim has given for oil of turpentine.



The other isomeric hydrocarbons of the terpene group have, doubtless, constitutions similar to those above given, differing from each other either by containing different radicals, or by the different positions of the latter.

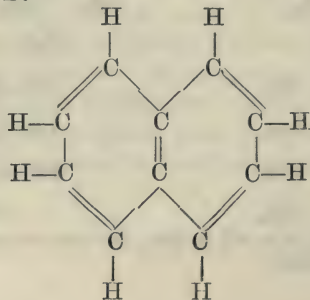
Besides the hydrocarbons containing one aromatic nucleus, there exist also several in which this group occurs twice or more times. As most of these bodies, however, are obtained by well-understood reactions, I need not discuss them here.

I only have to mention a most singular reaction by which some of them are formed, discovered by Zincke (*Ann. Chem. Pharm.*, clix, 367). This chemist intended to obtain dibenzyl by acting with finely-divided copper or zinc-dust upon benzyl chloride. In order to moderate the violent reaction, he diluted the benzyl chloride with ether and with paraffins, but under these circumstances no reaction took place. However, by employing aromatic hydrocarbons as diluents, action set in; but instead of dibenzyl being formed, he obtained a mixture of several other hydrocarbons, in the formation of which the aromatic hydrocarbons, in other respects so stable, take part with great energy. It is not possible to give an explanation of this fact, as all the products of this reaction have not yet been studied. But the fact exists that aromatic hydrocarbons, when heated with zinc-dust and benzyl chloride lose hydrogen and take part in the formation of new hydrocarbons. Thus, on employing benzene, one of the products is *diphenyl-methane* or *benzyl-benzene*,  $\text{CH}_2 \left\{ \begin{smallmatrix} \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_5 \end{smallmatrix} \right.$ , which is formed according to the equation—



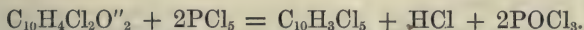
Further researches will no doubt throw more light upon this singular subject.

Amongst the products of the destructive distillation of coal and other substances, there always occurs *naphthalene*,  $\text{C}_{10}\text{H}_8$ , a hydrocarbon which in its chemical character bears so great a resemblance to benzene, that it must have a constitution very similar to the latter. Some years ago, Erlenmeyer pointed out that it had probably the following constitution:—



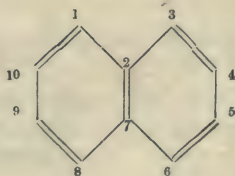
Naphthalene, therefore, would consist of two aromatic nuclei, which have two atoms of carbon in common. Graebe, who adopted this view, has proved the correctness of this hypothesis in a very ingenious way (*Ann. Chem. Pharm.*, cxlix, 21). His reasoning is as follows:—When naphthalene is oxidised, phthalic acid,  $C_6H_4(CO_2H)_2$ , is formed; this acid can be obtained in two different ways from naphthalene; viz., either by destroying the one or the other aromatic nucleus. Such an experiment cannot, of course, be made with naphthalene itself, because we have no means of distinguishing between the two groups. It appears, therefore, necessary, first, to replace hydrogen in one of the nuclei, and then find out which is attacked and which not.

On oxidising dichloronaphthaquinone,  $C_{10}H_4Cl_2O_2$ , phthalic acid is formed, a fact proving that in this quinone all the oxygen and chlorine are combined with those four atoms of carbon which are oxidised, the formula of dichloronaphthaquinone being, therefore,  $C_6H_4.C_4Cl_2O_2$ . By acting with phosphorous pentachloride on this compound, the dyad group,  $O_2$ , is replaced by chlorine, and, at the same time, one atom of hydrogen is substituted, pentachloronaphthalene being formed—



Now, if by the oxidation of pentachloronaphthalene the same carbon-atoms are attacked as in the quinone, monochloro-phthalic acid would be formed; but Graebe has shown that the product is tetrachlorophthalic acid, which proves that the second aromatic nucleus has now been destroyed, a complete proof that naphthalene has really the constitution assigned to it.

Whilst amongst the mono-substituted benzenes, no isomeric forms occur, we find that the monosubstitution products of naphthalene can exist in two isomeric modifications. This can also be easily explained from the constitution of this hydrocarbon. By representing it by two hexagons and numbering the corners, representing the carbon atoms—



we find that each of the atoms 1, 3, 6, and 8, is combined with another atom (2 or 7) in which all the combining units are saturated with carbon, whilst the atoms 4, 5, 9, and 10 are combined with carbon atoms to which hydrogen is attached. The functions of the atoms 1, 3, 6, and 8 will, therefore, differ from those of the four latter. This

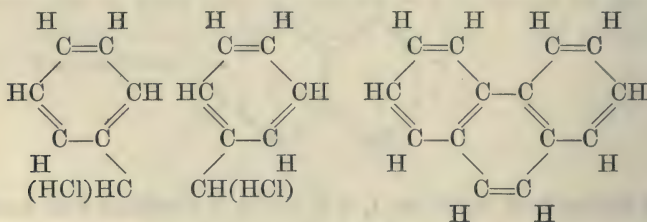
also explains the existence of two dinaphthyls, one of which has been obtained by the action of sodium upon monobrom-naphthalene, and the other by passing the vapour of naphthalene through a red-hot tube.

In most kinds of coal-tar containing naphthalene there occurs also *anthracene*,  $C_{14}H_{10}$ , a body exhibiting in its chemical relations great resemblance to benzene and naphthalene. The constitution of this hydrocarbon has been ascertained by Graebe and Liebermann by their beautiful researches on alizarin (*Ann. Chem. Pharm. Suppl.*, vii, 257).

Baeyer found that by heating phenols and compounds allied to them with zinc-dust, they are reduced to the hydrocarbon from which they are derived. By making use of this reaction, Graebe and Liebermann found that alizarin was a derivative of anthracene, and were thus enabled to effect for the first time the artificial preparation of a natural dye-stuff.

This example shows better than any other the correctness of the definition of organic chemistry "as the chemistry of the hydrocarbons and their derivatives."

The fact that alizarin is a derivative of anthracene enables us, as these chemists pointed out, to discuss the constitution of this hydrocarbon. From Limpricht's synthesis of anthracene from benzyl chloride it might be inferred that it is diphenyl-acetylene,  $C_6H_5.C \equiv C.C_6H_5$ . But this formula has to be rejected, because on oxidising alizarin we obtain phthalic acid; and as further benzene, naphthalene, and anthracene form a series, each member of which contains  $C_4H_2$  more than the preceding, it appears most probable that anthracene is built up from three aromatic nuclei in the same way as naphthalene from two. The formation of anthracene from two molecules of benzyl-chloride can now be easily explained. Each benzene nucleus loses one atom of hydrogen, and each of the groups  $CH_2Cl$  loses a molecule of hydrochloric acid, and the two residues  $C_6H_4.CH$  join together thus—



The complete reaction which takes place by heating benzyl chloride with water, takes place according to the equation—

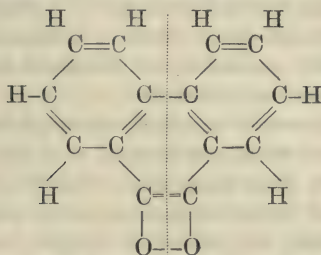




A further proof of the correctness of this view is, that by fusing anthraquinone with caustic potash, benzoic acid is formed.



The molecule of anthraquinone splitting up in the following way:—



The highest boiling portions of coal-tar contain, besides anthracene, two other hydrocarbons, *pyrene*  $\text{C}_{16}\text{H}_{10}$ , and *chrysene*  $\text{C}_{18}\text{H}_{12}$ , which have been also studied by Graebe and Liebermann (*Ann. Chem. Pharm.*, clviii, 285 and 299). They have found that these bodies exhibit in their chemical properties so close an analogy to anthracene, that their constitution must be very similar to that of the latter hydrocarbon. Both yield quinones on oxidation, which proves that they also consist of closed chains of carbon atoms. According to Liebermann, a similar constitution is possessed by *idrialene*,  $\text{C}_{22}\text{H}_{14}$ , a hydrocarbon occurring in idrialite, a mineral found in the mercury-mines of Idria (*Deut. Chem. Ges. Ber.*, iii, 154). This hydrocarbon forms the last member of a series which are derived from benzene by the successive addition of  $\text{C}_4\text{H}_2$ —

Benzene.....	$\text{C}_6\text{H}_6$ .
Naphthalene.....	$\text{C}_{10}\text{H}_8$ .
Anthracene .....	$\text{C}_{14}\text{H}_{10}$ .
Chrysene .....	$\text{C}_{18}\text{H}_{12}$ .
Idrialene .....	$\text{C}_{22}\text{H}_{14}$ .

Pyrene, which does not belong to this series, is isomeric with *diacetylenyl-phenyl*,  $\text{C}_6\text{H}_5.\text{C}\equiv\text{C}-\text{C}\equiv\text{C}.\text{C}_6\text{H}_5$ , a hydrocarbon discovered by Glaser, who has pointed out that of all known hydrocarbons it contains relatively the greatest amount of carbon, viz., 95 per cent., or more than coal or anthracite.

I have now finished my task, and have only to regret that the magnitude of the subject did not allow me to dwell longer on certain points, whilst others, such as Berthelot's remarkable researches on the formation of hydrocarbons at a high temperature, and the transformation of all carbon-compounds into hydrocarbons by means of hydriodic

acid, could not be mentioned at all. But the latter investigations alone would be sufficient to form the subject of a separate lecture.

There is perhaps no branch of our science which shows better the progress made by chemistry during the last thirty years, than that which I have brought before you to-night. And to what cause do we owe this rapid advance in our knowledge? I think this mainly due to the atomic theory, which found birth in Dalton's speculative mind, and has been gradually expanded and developed to its present state by the efforts of many eminent chemists.

But the atomic theory is generally accepted not only by chemists, but also by physicists, who have thought it of the greatest importance to find out the nature of an atom itself. Sir William Thomson has lately shown us how to solve a problem never dreamt of by chemists, viz., how to ascertain the absolute weight and size of an atom (*Nature*, 1871, Nos. 22, 31). Is it not, therefore, strange that we find chemists who desire to kick from under them the ladder by the aid of which, in no small degree, so great a progress has been achieved!

Such attempts are, however, not only of recent date. In opposition to Dalton and Berzelius, Wollaston introduced the term equivalent instead of atom. But whilst Dalton's original atomic weights were at the same time equivalents, the so-called equivalents of Wollaston's were no equivalents at all. By this a confusion arose between equivalent and atom, which was for a long time very detrimental to the progress of our science. It was only after Liebig had again pointed out the difference between equivalents and atoms, that theoretical chemistry advanced with rapid strides, and amongst those to whom we owe this speedy progress, I can only mention Laurent, Gerhardt, Williamson, Odling, and Kekulé.

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### XIII.—*Benzyl Isocyanate and Isocyanurate.*

By E. A. LETTS, Berlin University Laboratory.

THE first members of the group of compounds, now generally described as the isocyanates and isocyanurates, were discovered by Wurtz in the ethyl and methyl series. These bodies were called by him cyanic and cyanuric ether. They are, as is well known, obtained by the reaction of metallic cyanates on sulphovinates, and are decomposed by the elements of water into the corresponding amine and carbonic acid.

Later, Cloez discovered in the ethyl series an isomeric compound, which he designated by the name of cyanetholine; this is produced by the action of chloride of cyanogen on sodium alcoholate, and is decomposed by the elements of water into alcohol and cyanic acid (or rather the products of the latter's transformation), in consideration of which metamorphosis it must be viewed as the true cyanic ether (*Hofmann and Olshausen. Berichte der Deutschen Chemischen Gesellschaft*, 1870, p. 269). The recent researches of Hofmann and Olshausen make it probable that the body produced in the last mentioned transformation is the true cyanuric ether; in the methyl series at least this is certain.

In the aromatic series too there are many examples of this group of bodies; for instance, both the isocyanate and isocyanurate of phenyl are known, and side by side with them must be placed the singular compound known as phenyl isodicyanate, which is formed when phenylcyanate comes in contact with triethylphosphine. In the higher homologous series still more numerous examples may be expected. In the toluene group for instance, two different isomerides may be imagined, corresponding to each compound in the phenyl group, according as the benzene or methyl chains are influenced. Of the eight possible bodies thus producible only three have as yet been obtained, namely, isocyanate and isodicyanate of toluyl by Hofmann (*Berichte*, 1870, p. 656), and benzyl cyanurate by Cannizzaro (*Berichte*, 1870, p. 517).

The object of the following experiments was to supply some of the missing links in this chain of compounds:—

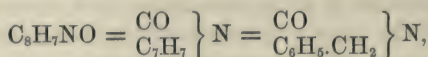
*Benzyl Isocyanate.*—If cyanate of silver be moistened with benzyl chloride and the mixture slightly warmed, pungent aromatic vapours are formed, causing the eyes to smart painfully, and having an odour which leave no doubt that the desired benzyl compound has been produced. For the preparation of a larger quantity of this body 100 grams of dry silver cyanate and 70 grams of benzyl chloride were submitted to distillation in a paraffin bath. Only 7—8 grams of a colourless, transparent liquid came over possessing the penetrating odour described. The operation was then proceeded with over the naked flame and the distillation commenced anew. The slightly yellow, oily liquid thus obtained solidified on cooling to a hard crystalline mass.

The colourless liquid is benzyl isocyanate, still, however, containing benzyl chloride. To free it from this impurity, distillation was resorted to, but owing to the slight difference between the boiling points of the two liquids it was found impossible to separate them by this means. The liquid boiled between  $175^{\circ}$  and  $200^{\circ}$ , and as the boiling point of benzyl chloride is  $175^{\circ}$ , it was hoped that at least the last portion of the distillate would be pure; but even this contained chlorine in perceptible quantity, and, besides, produced each time it was boiled a



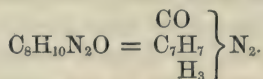
small quantity of the solid crystalline body; it was thus found impossible to obtain it in a state fit for analysis.

That it was really the compound



was clearly proved by its reactions, the products of which could be easily purified and analysed.

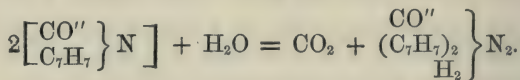
*Monobenzyl Urea*.—If the impure cyanate be treated with alcoholic ammonia, the mixture becomes heated and solidifies on cooling to a crystalline mass. If these crystals are again dissolved by warming the solution, water added, and the mixture boiled for a short time to get rid of any chloride of benzyl, beautiful long, white needles are obtained on cooling, consisting of monobenzyl urea—



	Theory.	Experiment.
C.....	64.0	64.2
H.....	6.6	6.8

This body is nearly insoluble in cold water, more soluble in hot water, and extremely so in alcohol. I have attempted, without success, to obtain a nitrate, but an insoluble platinum salt may be produced. The monobenzyl urea melts at 144°.

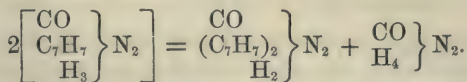
*Dibenzyl Urea*.—One of the most characteristic reactions of the cyanates generally is the transformation they undergo by treatment with water: carbonic acid is set free and a di-urea produced. The benzyl isocyanate likewise undergoes this metamorphosis; for if this compound be sealed up with water, in a tube, and heated for a couple of hours to 100°, a yellow oil, heavier than the water, is obtained, whilst on opening the tube carbonic acid escapes. When cold, the oily liquid solidifies into a crystalline mass. These crystals are the dibenzyl urea—



	Theory.	Experiment.
C.....	75.0	75.9
H.....	6.6	6.8

As will be seen on inspection, the numbers obtained agree only approximately with those required for the dibenzyl urea. I have not,

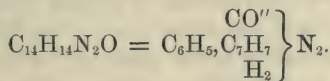
however, repeated the experiment, because dibenzyl urea has also been produced by Cannizzaro (*loc. cit.*) by heating monobenzyl urea :



I have repeated this experiment with the monobenzyl urea obtained from the cyanate, with exactly the same result, a body being produced having the appearance and properties of the dibenzyl urea obtained by treating the cyanate with water. I have, however, always remarked in this reaction the formation of more or less ammonia and cyanuric acid.

Regarding the properties of the dibenzyl urea I may further remark, that it is insoluble in water, but very soluble in alcohol, from which it crystallises in beautiful white needles. Like the monobenzyl urea, it forms a crystalline salt with platinum and hydrochloric acid, but no solid compounds with nitric or hydrochloric acid. It melts at 167°.

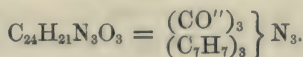
*Phenyl-benzyl Urea.*—Benzyl isocyanate mixed with aniline occasions an extrication of heat, and solidifies on cooling into a brown crystalline mass, which is purified by recrystallisation from alcohol. The body so prepared presents the form of white needles, insoluble in water and hydrochloric acid, which melt at 168°. They contain—



	Theory.	Experiment.
C.....	74·3	74·5
H.....	6·2	6·2

The mixed urea yields no crystallisable nitrate, but an insoluble platinum salt. On heating it, it shows the characteristic property of the ureas, evolving pungent fumes of benzyl isocyanate.

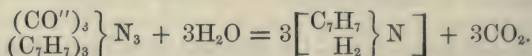
*Benzyl Isocyanurate.*—This compound is the principal product of the reaction of benzyl chloride on silver cyanate. The yellow, oily liquid before described as passing over at the latter stage of the distillation and solidifying on cooling, was treated with hot alcohol, in which it slowly dissolved. On cooling, beautiful silky needles were deposited from the solution, which, by a couple of recrystallisations from alcohol, are obtained pure. The analysis of these crystals showed that they possessed the composition of benzyl isocyanate. The boiling point lies so high that it could not be determined, and the other physical properties all characterize the isocyanurate—



	Theory.	Experiment.
C.....	72.2	72.4
H. ....	5.2	5.4

The extremely light needles of this body are insoluble in water, soluble with difficulty in ether, but more readily in alcohol, particularly if it be heated. They melt at 157° C. and boil above 320°.\* Sublimed several times in a tube they are decomposed into the isocyanate, known at once by the smell.

When fused with caustic potash they yield carbonic acid and benzylamine, identified by the analysis of its platinum double salt—



This reaction is characteristic for the isocyanurate.

The body obtained by Cannizzaro by the action of benzyl chloride on potassium cyanide, which, considering the mode of its production, must be regarded as the true cyanurate, possesses the same properties, so far as they have been observed, as the isocyanurate examined by myself. The melting point agrees nearly with that observed by Cannizzaro, being 153°. Are the two bodies obtained in such different ways isomeric or identical? The investigation of the products formed by the decomposition of Cannizzaro's compound by potash, which must give benzyl alcohol and cyanuric acid, can alone decide this question. Should the two, as certainly appears to be the case, be demonstrated as identical, it must be admitted that the cyanurate formed in the first instance has undergone the same change as Hofmann and Olshausen have observed in methyl cyanurate, which, by distillation, is converted into isocyanurate.

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#### XIV.—On a Compound of Sodium and Glycerin.

By E. A. LETTS, Berlin University Laboratory.

GLYCERIN being a triatomic alcohol, three compounds of this body with sodium should exist, in which respectively 1, 2, and 3 atoms of its typical hydrogen are replaced by the metal. In diatomic glycol the two sodium derivatives are easily produced; but hitherto with glycerin none of these bodies have been obtained. If a fragment of sodium be placed in glycerin, little or no action is observed, but on heating the

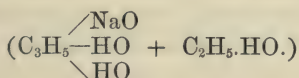
\* It has already been stated that the isocyanate is converted slowly into a solid crystalline body; it is probably the cyanurate, but this is only a supposition.



mixture a rapid extrication of hydrogen takes place, the sodium becomes red-hot, and the glycerin decomposed and charred, evolving fumes of acrolein. If, however, the sodium be diluted with mercury and then caused to act on glycerin, the action proceeds with more regularity, and finally a gummy mass is produced, which solidifies on cooling. If alcohol be now added, this gummy mass is not dissolved, but crumbles down into a white crystalline powder. The same body may be obtained by heating glycerin with dry sodium-alcohol: in this case, alcohol is set free, and a solid white substance remains.

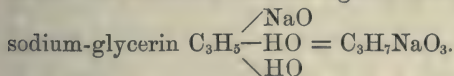
But the best method of preparing the compound, and one which yields it in any quantity, consists in dissolving sodium in alcohol and adding glycerin. At first no change is observed, but in a few minutes minute crystals consisting of radiating stars are formed, and in a short time a white crust is produced on the sides of the vessel. This crust is broken up, thrown on a filter, well washed with alcohol, and dried in a press between blotting paper. This must be done as quickly as possible, as the body is exceedingly deliquescent. The desiccation is afterwards completed over sulphuric acid, *but not in vacuo*.

The sodium in the compound thus prepared was estimated as sulphate, and amounted to 14·3 per cent.: a molecule of mono-sodium-glycerin + a molecule of alcohol requires 14·3 per cent. It, therefore, appeared that this body consisted of—



To ascertain if this alcohol merely acted as water, or rather alcohol, of crystallisation, 13·614 grams were heated in a current of dry hydrogen in a Liebig's drying tube immersed in boiling water: at the end of about three hours, the contents of the tube had lost 3·88 grams, representing 28·4 per cent. of the quantity taken: one molecule of alcohol = 28·7 per cent.

The sodium, carbon, and hydrogen were estimated in the body thus, dried: the numbers obtained agreed with those required for the mono-



	Obtained.	Calculated.
C	= 31·3	31·5
H	= 6·2	6·1
Na	= 19·9	20·1

The mono-sodium-glycerin is a white amorphous powder, attracting moisture with the greatest avidity from the air: by water it is con-

stantly decomposed into glycerin and hydrate of sodium. On heating it to a temperature of  $245^{\circ}\text{C.}$ , it shows signs of fusion, but appears to decompose at the same time. Bromine acts powerfully on it, giving small quantities of bromine derivatives, which I have not as yet studied. It is remarkable that in this reaction a large quantity of water is produced. Pentachloride of phosphorus, after a few moments' contact, also reacts with great energy, producing so much heat as to char the compound.

The principal product of its decomposition by heat appears to be acrolein.

In the hope of obtaining a cyanic compound of glycerin analogous to Cloez's cyanetholine (which he prepares by passing chloride of cyanogen into sodium alcoholate dissolved in alcohol), a current of this gas was passed over the mono-sodium-glycerin suspended in alcohol. The sodium became converted into chloride, the reaction occasioning an extrication of heat. On evaporating the alcoholic solution on a water-bath, a syrupy brown liquid was obtained of a sweet taste, and insoluble in ether. On attempting to distil this liquid, it decomposed with evolution of ammonia: treated with acids it effervesced.

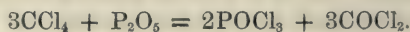
No method of purification presenting itself, the further examination of this body was abandoned.

XV.—*Notes from the Laboratory of the Andersonian University, Glasgow.*

By T. E. THORPE, Ph.D., F.R.S.E.

1. *On the Action of Phosphorus Pentasulphide on Carbon Tetrachloride.*

THE correspondence from St. Petersburg in the Journal of the Chemical Society of Berlin for January, 1872, contains a notice by Gustavson on the action of phosphoric anhydride on carbon tetrachloride. When 3 mols. of the tetrachloride and 1 mol. of phosphoric anhydride are heated for 48 hours in a sealed tube to about  $200^{\circ}$ — $210^{\circ}\text{C.}$ , the anhydride gradually disappears, and on opening the tube a large quantity of carbonyl dichloride is evolved, and the liquid portion consists mainly of phosphoryl trichloride. The reaction may be represented by the equation—



The fact that pentasulphide of phosphorus in many of its reactions is strictly analogous to the pentoxide, *e.g.*, in the production of sulphochloride of phosphorus by heating together phosphorus pentasulphide and pentachloride ( $3\text{PCl}_5 + \text{P}_2\text{S}_5 = 5\text{PSCl}_3$ ), corresponding to the formation of the oxychloride in the reaction,  $3\text{PCl}_5 + \text{P}_2\text{O}_5 = 5\text{POCl}_3$ , induced me to examine the action of this sulphide upon carbon tetrachloride. 23 grams of the tetrachloride and 11 grams of the phosphorus sulphide (the proportions required by the equation,  $3\text{CCl}_4 + \text{P}_2\text{S}_5 = 2\text{PSCl}_3 + 3\text{CSCl}_2$ ) were heated for a week in a sealed tube to  $200^\circ$ — $220^\circ$ , but not the slightest action was perceptible, and on opening the tube no escape of gas occurred; on distilling the mixture, very nearly the original amount of the carbon tetrachloride was recovered.

## 2. *On the Degree of Solubility of Silver Chloride in Strong Nitric Acid.*

It has been asserted by some experimenters, and denied by others, that strong nitric acid is able to dissolve very appreciable quantities of silver chloride, but hitherto, so far as I can learn, no exact quantitative determinations of the degree of the solubility have been made. It is important for several reasons that this uncertainty should be cleared up. Several of the most trustworthy estimations of atomic weights have been obtained by methods in which silver chloride was weighed after having been treated and washed with strong nitric acid. Thus Berlin determined the atomic weight of chromium by decomposing silver chromate dissolved in strong nitric acid; and Roscoe estimated the equivalent of vanadium from the decomposition of the oxychloride by water, strongly acidifying the liquid with nitric acid, precipitating the chlorine as silver chloride, and digesting the precipitate with strong nitric acid in order to remove the last traces of co-precipitated vanadic acid.

The following experiments, undertaken as an exercise in the method of weighing by vibrations, may serve to elucidate this point of the solvent action of strong nitric acid upon silver chloride.

A large quantity of the strongest nitric acid, apparently free from chlorine, and containing only a trace of sulphuric acid and iron, was cautiously distilled and the middle portion only of the distillate collected. This fraction was a second time carefully distilled, the first and last thirds being again rejected. By this treatment it was assumed that an acid would be obtained perfectly free from impurity (excluding other oxides of nitrogen), except such as it might take up by being in contact with glass. The lower oxides of nitrogen were in great part removed by aspirating through the liquid a current of washed air. In about 24 hours the dark colour of the acid was diminished until it had a scarcely perceptible yellow tinge. The greatest care was also taken



in the preparation of the silver chloride, the washing and drying being conducted by candle-light so as to maintain it perfectly white.

Two light and new flasks weighing about 17 grams, and of about 110 c.c. capacity, and made of the same variety of glass were cleaned and dried, and into one was placed about 0.01 gram of the finely powdered chloride. About 70—90 c.c. of the nitric acid was then poured into each, and the two flasks were kept side by side in a dark place, their mouths being closed by glass plates. They remained thus for ten days, during which time their contents were frequently agitated.

The temperature varied from  $15^{\circ}$ — $17^{\circ}$ . Two perfectly similar flasks both previously unused, were weighed one against the other by the method of vibrations, and into the one the greater part of the nitric acid resting over the silver chloride was decanted, and into the second about an equal quantity of the acid was poured from the other flask. The weight of the acid contained in each flask was then determined. The acid in both was next evaporated, the flasks being placed side by side on a layer of asbestos on wire gauze. The evaporation was carried on until about 5 c.c. of liquid remained: the flames were then lowered, and the acid vapours aspirated from the flasks by means of the Bunsen pump. In this manner the evaporation could be rapidly carried to complete dryness without ebullition and without danger of cracking the flasks.

The flasks were again transferred to the balance-case, and after standing a few hours were again weighed one against the other by the method of vibrations: the increase of weight corrected for the slight differences in the amount of acid evaporated, gave the amount of the silver chloride dissolved.

I. Excess of weight due to dissolved silver chloride .....	0.00143 gram.
Amount of nitric acid holding this quantity in solution .....	71.14 grams.

Hence 100,000 parts of nitric acid dissolved 2.01 parts silver chloride.

## II. Action of nitric acid containing lower oxides of nitrogen.

A quantity of the pure nitric acid was next saturated with the mixed oxides of nitrogen obtained by the action of nitric acid on arsenic-trioxide. The gases were washed by passing through a small quantity of nitric acid. The nitric acid remained in contact with the silver chloride for eight days. Temperature  $13^{\circ}$ — $16^{\circ}$ .

Increase of weight due to silver chloride	0.00175 gram.
Amount of nitric acid taken.....	95.08 „

Hence 100,000 of nitric acid containing lower oxides of nitrogen dissolve 1·85 parts of silver chloride.

3. *Action of Nitric Acid containing Lower Oxides of Nitrogen on Silver Chloride blackened by Exposure to Light.*

A quantity of pure silver chloride was exposed under water to active sunlight until it became nearly black, and it was then repeatedly washed with distilled water. Other details of experiment as in section I. Acid in contact with chloride during 14 days. Temperature 11°—16°.

Increased weight due to dissolved chloride .. 0.00078 gram.

Amount of acid used ..... 32·99 grams.

Hence 100,000 parts acid dissolve 0·84 parts of darkened silver chloride.

These experiments go to prove, therefore, that 100,000 parts of strong nitric acid dissolve about 2 parts of pure white silver chloride, and that the solubility is not sensibly affected by the presence of lower oxides of nitrogen in the acid; and that as the chloride darkens by exposure to light, still less of it is taken up by the acid, 100,000 parts of acid dissolving only 0·8 part of the blackened silver chloride.

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XVI.—*On the Estimation of Carbonic Acid in Sea-water.*

By Professor HIMLY.

HAVING been informed during my stay in London that a voyage round the globe for scientific purposes is in contemplation, and that the physical and chemical relations of sea-water will be included amongst the objects of research, I avail myself of the present opportunity of directing the attention of the Chemical Society to a circumstance which, so far as I know, has not been noticed elsewhere, namely, that the amount of carbonic acid in sea-water cannot be correctly determined by the ordinary gasometric method. The experiments of Dr. Jacobsen, Assistant in the Chemical Laboratory at Kiel, which he will shortly describe in detail, have shown that neither by boiling in a vacuum, nor by boiling at 100° under the ordinary atmospheric pressure, even when a stream of air freed from carbonic acid is simultaneously passed through the liquid, can the carbonic acid of sea-water be completely expelled. Indeed the quantity thus driven out is only a very small

fraction of the whole; but after about two-thirds of the liquid has been distilled over, a sudden evolution of gas takes place, and the greater part of the carbonic acid is given off with great rapidity. That the presence of magnesium chloride in the sea-water has an essential influence on the retention of the carbonic acid can scarcely be doubted.

It is clear, therefore, that to estimate the total amount of carbonic acid in sea-water, the gasometric method is insufficient, and that some other method must be devised.

For this purpose we may use baryta-water, or aqueous ammonia saturated with a suitable barium salt, and an ammonium salt. The following method of conducting the estimation is very simple, free from errors that might arise from the carbonic acid of the air, and very exact, inasmuch as it depends only upon two barium determinations.

The precipitation of the sulphuric and carbonic acid of the sea-water is performed in a graduated litre cylinder, with a quantity of the reagent, which need not be exactly known, but should be slightly in excess of that which is actually required. The liquid having been set aside, out of contact with the air, till the precipitate has completely settled down, an aliquot part,  $\frac{9}{10}$  for example, of the clear liquid is decanted; the barium contained in it is determined as sulphate; and from this the quantity of barium which remains dissolved in the last  $\frac{1}{10}$  of the liquid may be determined by calculation.

The barium carbonate is then dissolved by dilute acid, the liquid is filtered, and the total quantity of barium determined as sulphate. The difference gives the quantity of barium contained in the solution as carbonate, and from this the quantity of carbonic acid may be calculated.

To avoid loss of carbonic acid and other gases during and after the collection of the sea-water, I propose to add the reagent below the surface of the sea, and for this purpose I have devised an apparatus, of which, if agreeable to the Society, I will hereafter furnish a detailed description.\* In carrying out the mechanical details of such an apparatus, the advice of the well-known engineer, Dr. William Siemens, would, doubtless, be of very great value.

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\* The apparatus consists of a cylinder open at both ends, and capable of being closed when sunk to the required depth. For this purpose it is provided at each end with a large stopcock, which can be closed by a powerful spring, released at the proper moment by means of an electro-magnet, set in action in the usual way.



# ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

## Physical Chemistry.

**The Phenomenon of Affinity according to Multiples of Common Constants.** By JULIUS THOMSEN (Deut. Chem. Ges. Ber., v, 170—181).

THE object of this investigation is to show that, even in the case of quite different classes of compounds, the numbers expressing heat of combination are multiples of a constant, which does not differ greatly either way from 18,000.

Considering most of the determinations made by others as not sufficiently trustworthy, the author deduces this law, partly from his own experiments, partly from such results as have been found nearly identical by different observers. The following tables contain all the thermic reactions referred to in the paper:—

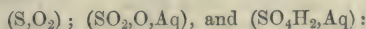
### *Oxides and Hydrated Oxides of Sulphur.*

(S, O <sub>2</sub> )	=	71072	=	4 × 17768	heat-units.*
(SO <sub>2</sub> , O, Aq)	=	71350	=	4 × 17837	„
(SO <sub>4</sub> , H <sub>2</sub> , Aq)	=	17848	=	1 × 17848	„
(SO <sub>2</sub> , O, H <sub>2</sub> O)	=	53502	=	3 × 17834	„
(S, O <sub>3</sub> , H <sub>2</sub> O)	=	124574	=	7 × 17796	„
(S, O <sub>3</sub> , Aq)	=	142422	=	8 × 17803	„

### *Oxides and Hydrated Oxides of Nitrogen.*

(N <sub>2</sub> O <sub>2</sub> O <sub>2</sub> )	=	39136	} Abnormal reactions.
(N <sub>2</sub> O <sub>4</sub> , Aq)	=	15505	
(N <sub>2</sub> O)	=	-18316	= -1 × 18316 heat-units.
(N <sub>2</sub> O <sub>4</sub> , Aq, O)	=	+18300	= +1 × 18300 "
(N <sub>2</sub> O <sub>2</sub> , O, Aq)	=	36341	= 2 × 18170 "
(N <sub>2</sub> O <sub>2</sub> , O <sub>2</sub> , Aq)	=	54641	= 3 × 18214 "
(N <sub>2</sub> O <sub>2</sub> , O <sub>3</sub> , Aq)	=	72941	= 4 × 18235 "

\* It may be noted that of the six reactions enumerated under this heading, only three have been made the subject of independent thermal measurements, namely, to use the author's notation—



the numbers given in the other cases are simply arithmetical deductions from these, thus:—

$$\begin{aligned} (SO_2, O, H_2O) &= (SO_2, O, Aq) - (SO_4, H_2, Aq), \\ (S, O_3, H_2O) &= (SO_2, O, Aq) + (S, O_2) - (SO_4, H_2, Aq), \\ (S, O_3, Aq) &= (SO_2, O, Aq) + (S, O_2). \end{aligned}$$

Further, it seems hardly safe to base any important theoretical conclusion upon a comparison of the quantity of heat developed in a reaction taking place between indefinite quantities of matter, such as the reaction (SO<sub>4</sub>, H<sub>2</sub>, Aq), with that produced in reactions taking place between atomic proportions of the reagents.—G. C. F.

*Sulphates.*

(Cu, O, SO <sub>3</sub> Aq)	=	56216	=	3 × 18705
* (Pb, O, SO <sub>3</sub> Aq)	=	75550	=	4 × 18888
(Fe, O, SO <sub>3</sub> Aq)	=	93861	=	5 × 18772
(Cd, O, SO <sub>3</sub> Aq)	=	54282	=	3 × 18094
(Zn, O, SO <sub>3</sub> Aq)	=	108460	=	6 × 18077
(Mg, O, SO <sub>3</sub> Aq)	=	180920	=	10 × 18092

The number for (SO<sub>2</sub>, O, Aq) was obtained from the known reactions (SO<sub>2</sub>Aq, Cl<sub>2</sub>) = 73906 heat-units, (SO<sub>2</sub>, Aq) = 7698 heat-units, (H, Cl, Aq) = 39315 heat-units, and (H<sub>2</sub>O) = 68376, and from the equations—

$$\begin{aligned} (\text{SO}_2, \text{Aq}) + (\text{SO}_2\text{Aq}, \text{Cl}_2) &= (\text{SO}_2, \text{Cl}_2, \text{Aq}) \\ (\text{SO}_2, \text{Cl}_2, \text{Aq}) &= (\text{SO}_2, \text{O}, \text{Aq}) + 2(\text{Cl}, \text{H}, \text{Aq}) - (\text{H}_2, \text{O}), \end{aligned}$$

which, by introducing the above values, give—

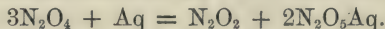
$$7698 \text{ heat-units} + 73906 \text{ heat-units} = (\text{SO}_2, \text{O}, \text{Aq}) + 78630 \text{ heat-units} - 68376 \text{ heat-units},$$

therefore—

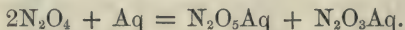
$$(\text{SO}_2, \text{O}, \text{Aq}) = 71350 \text{ heat-units}.$$

In the nitrogen series the first two numbers do not seem to contain the constant 18,000. But the number obtained by their addition, and expressing the reaction (N<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>, Aq), is a multiple of 18214. This is probably due to secondary reactions, which increase the heat due to the reaction (N<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>) by as much as they diminish the heat due to the reaction (N<sub>2</sub>O<sub>4</sub>, Aq), these secondary reactions being caused in the first case by a partial decomposition (dissociation) of the nitrogen tetroxide, and in the second by the disappearance of this anomalous state during the solution in water.

The thermic reactions of N<sub>2</sub>O<sub>4</sub> indicate that its decomposition by water must not be represented by the equation which is commonly given, namely,—



but by the following,



The tables show that the value of the constant for copper, lead, and iron, is somewhat greater than for cadmium, zinc, and magnesium.

With regard to the oxides of manganese, the author has succeeded in establishing that the value of the constant does not differ much from 18000, and that for every additional atom of oxygen in the oxide, the total heat of combination is *diminished* by about 18000 heat-units. This is exactly the opposite to what takes place in the nitrogen series, where for every additional atom of oxygen the heat of combination *increases* by the constant quantity of 18260 heat units.

The question whether there exists more than one constant cannot be answered *à priori*, whilst it can scarcely be doubted that more exact experiments would prove the constants deduced in this paper to be identical.

\* Supposed in aqueous solution.

The determination of the constant 18000 was facilitated by the fact that in some of the cases considered in this paper the thermic reaction is represented by this constant itself.

Should it be proved that the chemical affinities coming into play in the formation of analogous compounds, and measured by the number of heat-units evolved, can in many other cases be expressed as multiples of certain constants, our conception of the condition of the atoms would gain considerably in distinctness. If, further, it should be shown that with many other compounds, besides those of the oxides of nitrogen and of manganese, the addition of an atom of oxygen causes, according to the nature of the radical, either a constant increase, or constant diminution, of the total heat of combination, a condition of the molecular forces would be indicated analogous to that supposed by the electrochemical theory.

Finally the author refers to a paper published by him in the year 1854 (*Pogg. Ann.*, vol. 92, p. 44), in which he had clearly stated the principle of multiples with regard to chemical affinity.

R. S.

**Criticism of the Numbers calculated by Berthelot in his Papers**—*Sur la Chaleur de Formation des Azotates, Sur la Chaleur de Formation des Composés Oxygénés de l'Azote, etc.* By JULIUS THOMSEN (*Deut. Chem. Ges. Ber.*, v, 181—185).

IN the first of the above papers Berthelot makes use of certain numbers obtained by Bunsen and Schischkoff for the heat of combustion of gun-powder, in order to calculate the heat of formation of nitric oxide, denoted by  $y$ , from the following equations—

$$(1) \quad 169000 \text{ heat-units} = 0.037 y = 61500 \text{ heat-units} + 102400 \text{ heat-units} + 0.781 y.$$

Or—

$$(2) \quad 169000 \text{ heat-units} - 163900 \text{ heat-units} = 0.744 y.$$

from which follows—

$$y = 6900 \text{ heat-units.}$$

The value of  $y$  is here calculated from two numbers differing from each other only by 3 per cent., so that an error of only 3 per cent. in the determinations from which they are derived would either double the value of  $y$ , or reduce it to nothing.

Now Berthelot's calculation involves the following determination by Favre, made with the mercury-calorimeter,  $\frac{1}{2}(\text{N}_2\text{O}_2, \text{O}_3, \text{Aq}) = 20700$  heat-units; and the author, who for the same reaction had found  $\frac{1}{2}(\text{N}_2\text{O}_2, \text{O}_3, \text{Aq}) = 36470$  heat-units, shows that merely by correcting Favre's number, the equation (1) would give, not  $y = 6900$ , but  $y = -8870$ .

In the second paper Berthelot makes use of another of Favre's determinations,  $\frac{1}{2}(\text{N}_2\text{O}_2, \text{O}, \text{Aq}) = -6600$  heat-units. The author, however, who from his own experiments had found  $\frac{1}{2}(\text{N}_2\text{O}_2, \text{O}, \text{Aq}) = +18170$  heat-units, considers all numbers calculated by Berthelot from Favre's number as completely useless. But he especially finds fault with Berthelot's determination of the reaction  $(\text{NO}, \text{O})$ , inasmuch



as it is derived, not from direct experiment, but merely from hypothetical considerations. His own results with regard to this reaction, obtained by direct experiment, differ very widely from the calculated result of Berthelot, as is seen from the following:—

$$(\text{NO}, \text{O}) = \begin{cases} + 3000 \text{ heat-units} \dots & \text{Berthelot.} \\ + 19568 \quad \quad \quad \text{,,} \quad \dots & \text{Thomsen.} \end{cases}$$

R. S.

### **Influence of a Change of Specific Gravity upon Melting Point.**

By F. MOHR (Ann. Chem. Pharm., clxii, 61—67).

IN accordance with the mechanical theory of affinity, which requires that the melting point be raised or lowered according as the specific gravity is increased or diminished, the author has found by experiment that, in the case of garnets, fusion lowers the melting point at the same time that it diminishes the specific gravity. The remainder of the paper contains theoretical considerations.

R. S.

### **Reciprocal Action of Acids and Alkalis in Solution when separated by a Porous Diaphragm.** By ED. LANDRIN (Compt. rend., lxxiv, 681).

IN studying the causes which influence the diffusion of bodies across a porous partition, the author was led to experiment on solutions of acids and alkalis.

In an exterior vessel, 100 c.c. of an alkaline solution of known strength was placed; and 60 c.c. of an acid solution, whose strength was also known, was put into a Bunsen's porous cell, within the first. Diffusion went on for 24 hours. At the end of that time the quantities of uncombined acid and alkali were determined, and the amount of combination that had taken place was calculated by difference. Experiments were made on solutions of hydrochloric acid, sulphuric acid, and nitric acid, with solutions of potash, soda, potassium carbonate, and sodium carbonate.

The numbers found to represent the rates of diffusion for each pair of bodies correspond sensibly with those which have long been considered to represent the relative electrical attractions of those substances. For example, potash combines more energetically with sulphuric acid than with hydrochloric acid or nitric acid; and a corresponding rate of diffusion of potash into the solution of sulphuric acid, as compared with the rates of diffusion of that body into solutions of the other acids, was found. Again, the rates of diffusion for the carbonates of potassium and sodium into the acid solutions are less than those for the free bases. The explanation of this is, of course, that a certain amount of energy, which would otherwise assist the diffusion, is required for the liberation of the base from the acid portion of the salt.

A table of numbers is given by M. Landrin; but unfortunately the results are not stated in absolute measure; nor in a form from which absolute results can be calculated.

J. T. B.

**The Decomposition of Water by Zinc in Conjunction with a more Negative Metal.** By J. H. GLADSTONE and ALFRED TRIBE (Proc. Roy. Soc., vol. xx, 218).

PURE zinc is incapable of decomposing pure water, even at  $100^{\circ}\text{C}$ ., but at a considerably higher temperature it is known to combine with its oxygen. Davy exposed pure water for two days to the action of a pile of silver and zinc plates, separated only by pasteboard, without obtaining any hydrogen. Buff has shown that a very minute trace of gas can be formed at the ordinary temperature in a vacuum by a pair of zinc and platinum plates.

It occurred to the authors to ascertain whether, by bringing the two metals closer together, and so increasing the electrical tension of the liquid, the same combination of zinc with oxygen could be effected at the ordinary temperature, which takes place without the second metal at a very high temperature.

Some zinc-foil was allowed to remain in a somewhat dilute solution of copper sulphate, until its surface was well covered with spongy copper. The metals were thoroughly washed with distilled water, and then they were immersed in a bottle of distilled water with a delivery tube. Minute bubbles of gas quickly made their appearance, which proved to be hydrogen, and zinc oxide was formed. Two experiments were made quantitatively, the gas being collected and measured at the end of every 24 or 48 hours.

In experiment A, 33·4 grms. of zinc-foil were employed, 2·6 meters long and 0·05 wide. The coils were kept apart by muslin. In experiment B there was used 1 meter of similar foil crumpled up.

The two experiments evidently continued almost *pari passu* for months, the amount of hydrogen gradually diminishing. Subjoined are the results of the first and last observations:—

Day.	Mean temp. °C.	Expt. A. c.c.	Expt. B. c.c.
1	12·8	117·1	49·6
84	10·0	14·0	5·1

Under the microscope the bubbles of gas are seen to form, not on the zinc, but among the copper crystals, and sometimes to make their appearance on the glass at some distance off.

From the position of platinum in the electro-chemical series, it was anticipated that the effect would be still more marked with that metal in a spongy state on the zinc. The metal was deposited from the tetrachloride, and, of course, thoroughly washed. There was only 0·6 meter of foil, but the following quantities of hydrogen were obtained:—

Day.	Mean temp. °C.	Vol. in c.c.
1	11·7	143·6
8	7·7	12·3

Lest it might be contended that the free oxygen usually present in distilled water had been the means of starting this action, the experiment was repeated with water as free from oxygen as could be obtained

by boiling. One meter of the same zinc-foil, covered with copper, was employed, and the result was nearly as before, 40 c.c. of gas being obtained the first day. This arrangement was taken advantage of to examine the effect of a high temperature. Without removing the delivery tube, the contents of the flask were heated to near  $100^{\circ}\text{C}$ ., when 123.5 c.c. of hydrogen were given off in ten minutes. The apparatus was allowed to cool, with the mouth of the tube under water, when the production of gas became small again, and, after two days, it was again heated nearly to the boiling-point, when it gave off 93.4 c.c. in ten minutes; after another period of two days it gave 64.1 c.c.; and after three days more, 132.1 c.c. in the first thirty minutes, 108.4 in the second thirty minutes, 94.3 in the third, and 89.9 in the fourth. The capacity of the flask was three ounces.

Iron and lead, under similar circumstances, also decomposed pure water, and the action of magnesium was greatly increased by conjunction with copper. The effect of the more negative metal was the same as would have been produced by an increase of heat.

In a practical point of view this experiment may serve as a ready means of preparing pure hydrogen; in a theoretical point of view its interest seems to lie in the fact that the decomposition of a binary compound by means of two metals, may take place at infinitesimally short distances, when it would not take place were the layer of liquid enough to offer resistance to the current, and also in the correlation between this force and heat.

As might be expected, zinc in conjunction with copper is capable of decomposing other liquids than water. Chloroform yields readily to its power, and iodide of ethyl (which Prof. Frankland decomposed by zinc only at a great heat) is split up rapidly at the ordinary temperature.

A. T.

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### Absorption Spectra of Chlorine and Chloride of Iodine. By D. GERNEZ (Comp. rend., lxxiv, 660—662).

THE spectra of various coloured vapours, nitrogen tetroxide, bromine, iodine, chlorine trioxide, chlorine tetroxide, and manganese perchloride, have been described by Brewster, W. H. Miller, and W. A. Miller. A thickness of a few centimeters of these vapours shows the characteristic lines of their spectra well. But this is not the case with chlorine, of which a column 150 centimeters long gives but a faint effect, and in the case of iodine chloride a column of a considerable length is also required to exhibit the spectrum well. M. Gernez has, however, examined the spectra of these bodies.

To examine the spectrum of chlorine, he took a tube 6 centimeters in diameter and 4.68 meters long, closed at its ends with parallel plates of glass. Since in a column of such dimensions a very small quantity of chlorine trioxide or tetroxide would be sufficient to bring out the absorption spectra of these gases, it was necessary to take every precaution to obtain the chlorine in a pure state. The gas was liberated from hydrochloric acid by manganese dioxide, and was passed through a tube of glass kept at a red heat, so as to destroy any small quantity of the oxychlorides that might be present. The experimental



tube was then filled with it by displacement. A beam from a lime light was passed along the axis of the tube. This, on emerging, fell on the slit of a spectroscope with two prisms, and gave a very well marked spectrum.

The spectroscope with two prisms was employed, because, while no advantage is gained in spreading out the absorption-spectrum of a liquid, the opposite is the case with the absorption-spectrum of a gas. When the absorption-spectrum of a liquid is spread out by using more than one prism, the bands only become broader and fainter, but in the case of a gas the lines do not lose intensity, while they gain very much in distinctness.

The spectrum of chlorine extends to the violet, and possesses well marked lines. From the less refrangible end up to the D line it is continuous; but from a position a little beyond that, begins a series of five nearly equidistant lines analogous to those observed in the spectra of bromine and iodine. The intensity and appearance of these lines vary from place to place along the spectrum. They extend up to the violet, and the violet was completely absorbed in the case of the source of light employed.

The monochloride of iodine is more easily managed than chlorine. At 40° C. this body gives off so much vapour that a thickness of 30 c.m. of it is sufficient to produce an absorption-spectrum. It consists of a score of fine lines between the extreme red end and a point a little beyond the line D, nearly equidistant, and of sensibly equal intensity. There are also two other intense lines in the yellow. No others are observable throughout the spectrum.

The system of lines resembles those of the iodine spectrum more than those of the chlorine spectrum. It differs, however, from the iodine spectrum in the absence of the lines in the green, and in the fact that the lines of the chloride of iodine commence sensibly nearer to the red end than do those of the iodine spectrum.

J. T. B.

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**On the Contraction of Solutions of Cane Sugar at the moment of Inversion, and on a New Process of Saccharimetry.** By G. CHANCEL (*Compt. rend.*, lxxiv, 376—378).

It has been shown by Graham that solutions of sugar undergo contraction when they are inverted, but the amount of that contraction has not hitherto been the subject of accurate measurement. The apparatus employed by the author in the following experiments consisted of a flask measuring from 50—100 c.c., to which was fused a tube of 1—2 mm. internal diameter, and about 200 mm. long, and having a cylinder of 12—15 mm. fused to its upper extremity. The narrow tube was calibrated and divided into parts of equal capacity. The capacity of the flask and tube was determined with care.

A known quantity of cane sugar dissolved in water was put into the flask and cooled to zero, mixed with 1 per cent. of sulphuric acid diluted with water, and made up with water to the zero mark in the narrow tube, while the whole remained in ice. The apparatus

was then sealed and heated in the water-bath for eight or ten minutes, and again cooled to zero, and the new volume noted. The apparatus being then refilled with a solution of pure sugar of the same strength as that originally employed, and weighed, the density of the unaltered solution was found, and from this and the observed contraction the following tables have been calculated.

The author further proposes to determine the proportion of sugar in a saccharine solution by observing the diminution of volume occurring on inversion.

TABLE I.

Percentage of sugar in the solution.	Density at zero of the solution.		Percentage of sugar in the solution.	Density at zero of the solution.	
	Of cane-sugar.	Of invert-sugar.		Of cane-sugar.	Of invert-sugar.
	Diff.	Diff.		Diff.	Diff.
0	1·0000	40	13	1·0542	44
1	1·0040	40	14	1·0586	44
2	1·0080	41	15	1·0630	44
3	1·0121	41	16	1·0674	44
4	1·0162	41	17	1·0718	44
5	1·0203	41	18	1·0763	45
6	1·0244	41	19	1·0808	45
7	1·0286	42	20	1·0854	46
8	1·0328	42	21	1·0900	46
9	1·0370	42	22	1·0946	46
10	1·0413	43	23	1·0992	46
11	1·0456	43	24	1·0039	47
12	1·0499	43	25	1·0086	47
13	1·0542	43			

TABLE II.

Cane-sugar in 100 parts.	Volume at 0° after inversion.	Contraction.	Cane-sugar in 100 parts.	Volume at 0° after inversion.	Contraction.
0	1·00000	0·00000	13	0·99680	0·00320
1	0·99971	0·00029	14	0·99659	1·00341
2	0·99943	0·00057	15	0·99639	0·00361
3	0·99916	0·00084	16	0·99620	0·00380
4	0·99889	0·00111	17	0·99601	0·00399
5	0·99863	0·00137	18	0·99582	0·00418
6	0·99838	0·00162	19	0·99564	0·00436
7	0·99814	0·00186	20	0·99546	0·00454
8	0·99790	0·00210	21	0·99528	0·00472
9	0·99767	0·00233	22	0·99511	0·00489
10	0·99744	0·00256	23	0·99495	0·00505
11	0·99722	0·00278	24	0·99478	0·00522
12	0·99701	0·00299	25	0·99462	0·00538

## Inorganic Chemistry.

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### Action of Low Temperatures on the so-called Supersaturated Solutions of Sodium Sulphate. By L. C. DE COPPET.

THE author points out that the supposed hydrate of sodium sulphate, which Tomlinson and Violette describe as being deposited at temperatures below 26° F. in the form of a white powder, is really *ice* mixed with variable quantities of the seven-atom salt. He also points out another error which occurs in several of Mr. Tomlinson's papers. The crystals of sodium sulphate resembling octohedrons which separate from a saturated solution, when cooled to a sufficiently low temperature are called *anhydrous*: they are, however, crystals of the seven-atom salt, the original prismatic form being so modified by the large development of certain faces that they may be easily mistaken for crystals of the cubic system.

S. W.

### On the Proportion of Ozone contained in the Air of the Country, and on its Origin. By A. HOUZEAU (Compt. rend., lxxiv, 712—715).

THE author concludes from quantitative research that the air of the country at 2 meters from the ground contains a maximum of  $\frac{1}{450,000}$  of its weight of ozone, or  $\frac{1}{700,000}$  of its volume. The usual test-paper was employed (papier de tournesol vineux mi-ioduré). He refers the production of this body to the continuous electrical action which goes on between the clouds and the earth.

S. W.

### Facts for the History of Nitrification. Composition of the Soil of Tantah (Lower Egypt). By AUGUSTE HOUZEAU (Ann. Chim. Phys. [4], xxv, 161—167).

TANTAH is a town situated in the Delta of the Nile, of the mud of which its houses are built. They stand upon mounds formed of the ruins of a series of former ones. Each house affords shelter, not only to the family, but also to the ox, cow, and ass of the peasant, by whom the deep soil of these mounds is dug up for manure. This soil and the surface-soil the author has analysed, in the hope of throwing further light upon the process of nitrification.

Both soils were of a deep guano-yellow colour, inodorous, tasteless, and neutral to test-paper, contained ammoniacal salts and nitrates, and yielded a red ash free from carbonates. The surface-soil contained a good deal of straw and some green organic matter soluble in alcohol, while the deep or ancient soil contained only a little straw and a very little greenish-yellow organic matter. The recent soil contained 14.276 per cent of moisture, and the ancient, 10.719 per cent. Further details of the composition of the two soils are included in the annexed table, the soils having been dried at 110° for analysis.



	Recent soil.	Ancient soil.
Organic matter .....	9.915	4.308
Clay, silica, oxide of iron, magne- sium, and iron phosphate.....	84.093	89.605
Soluble chloride, equivalent to sodium chloride .....	5.147	4.520
Calcium sulphate .....	0.015	0.129
Nitric acid of the nitrates.....	0.171	0.949
Ammonia ready formed .....	0.039	0.365
Nitrogen of the organic matter ....	0.620	0.124
	<hr/> 100.000	<hr/> 100.000
Total nitrogen .....	0.696	0.670

From this table it is seen that in the ancient soil half the organic matter has disappeared, and that the quantity of the nitrogen has not changed, but that the quantity of ammonia nitrate has increased ten-fold at the expense of the organic matter.

This investigation exhibits the process of nitrification in the absence of alkaline bases. Had these been present, as the editors of the *Annales* point out, the ammonia would no doubt have been also converted into nitrates.

E. D.

### Iron, Crystalline or Burnt. By H. CARON (Compt. rend., lxxiv, 662—664).

THE object of this paper is to examine into some questions relative to the brittle state of iron. It seemed to the author probable that some of the theories held at present on the subject are the results of imperfect observations, and his experiments were undertaken with a view to prove or disprove them.

When a bar of iron of good quality, fibrous and tenacious, is allowed to cool in the air, without being hammered, it becomes brittle after having been raised to a white heat, and on fracture presents a laminated crystalline appearance. The iron is then said to be *burned*, and it is generally supposed to have absorbed oxygen.

Experiments, in the way of analysis, failed to show whether this is the case or not. There is always a certain quantity of oxygen and other impurities in iron, but the quantities are so small, both in good iron and in burnt iron, that the results of the analysis did not appear conclusive on the question.

Accordingly the following direct experiment was tried. A bar of *Franche-Comté* iron, whose quality as to strength and fibrous structure had been previously ascertained, was cut up, and the pieces were heated to whiteness. Some of them were heated in the furnace of an ordinary forge, others were placed in a porcelain tube, and were heated while a current of nitrogen was passing over them, and some were similarly exposed to a high temperature in a current of hydrogen. After cooling all the pieces presented the same crystalline appearance on fracture. Forged at a red heat, or broken cold, they all possessed

sensibly the same properties, and the same defects. Heated to whiteness they all had their primitive qualities similarly restored. It appears thus, that burnt iron is obtained equally when iron is heated in air, in a neutral, and in a reducing atmosphere, and it seems scarcely admissible that the deterioration of the metal is due to the absorption of any gas. Doubtless it is due simply to the action of heat modifying its molecular condition.

M. Caron also experimented on the question whether the cold of our winters renders iron crystalline and brittle. He does not consider that the fact of there being more breakages during frosty weather, if it be a fact, is enough to prove that iron really becomes crystalline during the cold. If this be used as a proof it would be necessary to suppose also that iron crystalline at  $-20^{\circ}\text{C}$ . would again become fibrous when the temperature rises to  $+20^{\circ}\text{C}$ .

The experiments that he tried were on pieces of the bar iron above mentioned; some of them were exposed to a freezing apparatus, and kept at varying temperatures from  $0^{\circ}$  to  $-18^{\circ}\text{C}$ . for three months; others were exposed to the winter's cold, and they were afterwards broken, some of them while cold, others when they had wholly and partially returned to ordinary temperatures. Not one of them showed any diminution in strength, or any appearance of taking a crystalline form.\*

The author remarks, however, that he made no experiments on any but good iron.

The consequence of his observations M. Caron considers to be, that whenever a broken bar of iron exhibits a crystalline structure, we may be quite sure that the fault has existed from the beginning, and that neither cold, nor work that it has been exposed to after its fabrication, is capable of bringing fibrous iron into this form.

J. T. B.

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## Mineralogical Chemistry.

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**Analysis of Bauxite from the Wochein (Austria).** By EDMUND DRECHSTER (Dingl. Polyt. Jour., cccii, 479—481).

THE mineral possesses slight hardness, and may be divided into two portions, one of dark red colour, the other light red.

By treatment with concentrated sulphuric acid, under ordinary circumstances, only slow decomposition results, and there remains, after one treatment with the acid, a residue amounting to 14 per cent., which, however, may be further dissolved by fresh digestion with acid.

By fusion with potassium sulphate, or treatment with sulphuric acid in sealed glass tubes, this bauxite is easily and entirely decomposed.

Samples of the dark and light coloured portions of the mineral were selected, and separately analysed, yielding results as follows:—

\* This result agrees perfectly with the recent experiments of Dr. Joule (*Proc. Manchester Phil. Soc.*, 1871, and this Journal, 1871, p. 445).—J. T. B.

	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	SiO <sub>2</sub> .	H <sub>2</sub> O.	K <sub>2</sub> O	Na <sub>2</sub> O	Li <sub>2</sub> O.	TiO <sub>2</sub> .
Dark ..	63.16	23.55	4.15	8.34	0.79		trace =	99.99
Light ..	72.87	13.49	4.25	8.50	0.78		trace =	99.89

This analysis, which gave results similar to those which were obtained several years ago on the bauxite from Feistritz, in Oberkrain, shows that the amount of alumina contained in the bauxite from the Wochein is very high, which makes it a very valuable mineral for the production of alumina compounds, as alum, sodium aluminate, aluminium sulphate, &c. On the other hand, the samples of the Krain bauxite analysed by us contained much ferric oxide, which would exert a prejudicial influence in its use in chemical industry.

W. S.

### The Amblygonite of Montebras.

ANALYSES of this mineral by Rammelsberg (*Deut. Chem. Ges. Ber.*, v, 78), and by v. Kobell (*J. pr. Chem.* [2], v, 112), have confirmed the result of Pisani's analysis (p. 126 of this volume), namely, that it is not a distinct species, as supposed by Moissenet, but identical with the amblygonite from Penig, in Saxony, and from the United States. The following are the results of analysis:—

	From Montebras.			From Penig.
	Pisani.	v. Kobell.	Rammelsberg.	Rammelsberg.
Fluorine .....	8.20	9.00	10.06	9.44
Phosphoric anhydride....	46.15	45.91	48.55	48.00
Alumina .....	33.82	35.50	36.36	36.26
Lithia .....	8.10	6.70	7.96	6.68
Soda.....	2.28	5.30	0.93	3.29
Potash.....	—	—	0.40	0.43
Lime.....	—	0.50	—	—
Manganese oxide .....	0.40	—	—	—
Silica .....	—	0.60	—	—
Loss by ignition .....	1.10	0.70	—	—
	100.05	104.21	104.26	104.10

To separate the lithium and sodium, v. Kobell heats the chlorides of these metals to incipient fusion, in a weighed platinum capsule; then weighs the chlorides; leaves them exposed for 24 hours to an atmosphere not moist enough to act on the sodium chloride, till the lithium chloride has absorbed water; drenches the partly deliquesced mass with alcohol; decants carefully; repeats the washing and decantation a second time; and weighs the residual sodium chloride. An experiment on weighed quantities of the mixed chlorides showed that this method gives exact results.

H. W.



**Fossil Resin from the Val d'Arno Superiore.** By ICILIO GUARESCHI (Il Nuovo Cimento [2], v—vi, 175—185).

THE lignites of the Figline basin on the left bank of the Arno contain several fossil resins, one of which is called by the country people "combustible earth" (*terra che brucia*).

This resin is a light, very friable, amorphous, yellowish-white mass, which burns like touchwood with a somewhat smoky flame. It contains 41·3 p. c. organic, and 58·7 mineral substance, the latter consisting of silica, ferric oxide, alumina, manganese oxide (trace), lime, magnesia, potash, and soda, soluble in hydrochloric acid; and silica, iron, silicate, and aluminium silicate, insoluble in that acid.

The organic matter is almost wholly soluble in alcohol, and may be resolved, by fractional solution in that liquid, into two resins,  $\alpha$  and  $\beta$ , having the following composition:—

	Resin $\alpha$ .	Resin $\beta$ .
Carbon .....	72·72	76·94
Hydrogen .....	9·41	9·12
Oxygen .....	17·87	13·94
	<hr/> 100·00	<hr/> 100·00

The composition of  $\alpha$  agrees nearly with the formula  $C_{40}H_{64}O_8$ , that of  $\beta$  with  $C_{40}H_{58}O_6$ .

The author supposes the resin  $\alpha$  to have been formed by oxidation of a polymeride of turpentine oil.  $4C_{10}H_{16} + O_8 = C_{40}H_{64}O_8$ , and  $\beta$  by abstraction of the elements of water from  $\alpha$ :  $C_{40}H_{64}O_8 - 3H_2O = C_{46}H_{58}O_6$ . Both exhibit considerable analogy, both geologically and chemically, to the group of resins called pyropissite, from the lignite of Weissenfels.

Resin  $\alpha$  is blackish when melted, yellowish in powder, lighter than water, softens at 75°, and melts completely at 90°. It dissolves with brown colour in alcohol, and with great facility in benzene and turpentine oil, very slightly in ether. Strong sulphuric acid dissolves it in the cold, more easily when heated. Nitric acid acts but slightly or not at all upon the resin itself, but when added to the sulphuric acid solution it appears to form a nitro-substitution product. By melting the resin with potash, no organic acid is formed, but merely an alkaline carbonate. The resin, when submitted to dry distillation, yields a brown empyreumatic liquid, which does not appear to contain succinic acid.

Resin  $\beta$  is blackish and amorphous, very slightly soluble in alcohol, much more freely in benzene and turpentine oil. It is lighter than water, melts at a temperature above 120°, and is insoluble in potash.

H. W.

**Gases of Solfataras.** By GORCEIX (Ann. Chim. Phys. [4], xxv, 559—566).

THE author, in a recent visit to Vesuvius and the Phlegreæan Fields, made numerous analyses of the volcanic gases. A few of his results are subjoined.

Source.	CO <sub>2</sub> .	H <sub>2</sub> S.	O.	N.	Temperature.
Great Solfatara .....	88·8	7·0	0·7	4·5	110° to 120°
Stufa, E. ....	29·5	traces	13·2	57·3	25°
Lago d'Agnano .....	96·1	—	—	—	—
Grotto del Cane .....	77·0	—	—	—	—
Acqua ferrata del Pozelio (Castel- lamare).....	29·1	00·0	0·7	70·2	{ Air, 28° Water, 25°

At Vesuvius aqueous vapours containing carbon dioxide, besides dry emanations of hydrochloric acid and sulphurous oxide without carbon dioxide, at a temperature of 225°, were evolved from the crater and from fissures on the sides. From the great Solfatara there issued with much noise a mixture of steam, hydrogen sulphide, carbon dioxide, and air. The sides of the cavity were covered with crystals of sulphur and sulphide of arsenic.

C. G. S.

## Organic Chemistry.

### On Differences of Boiling Point in Homologous Series. By E. LINNEMANN (Ann. Chem. Pharm., clxii, 39).

KOPF has concluded from his experiments that the differences in boiling point between consecutive members of a homologous series are equal. The author, on the other hand, concludes that this law is not true, even within some considerable limits of variation. By repeated distillation in the platinum-gauge apparatus formerly described, the boiling points of a number of substances were carefully determined, all superheating of vapour being avoided, and great degrees of purity obtained. After correction and reduction, different specimens gave boiling points rarely varying from one another by more than 0·1°, the mean difference observed in 25 determinations of 11 substances being 0·09°. Hence great accuracy is obtainable by the use of this apparatus.

A considerable number of boiling points were thus determined, with the following results:—

Chlorides.				Bromides.			Iodides.		
	Boiling point.	Differ-ence.	De-crease.	Boiling point.	Differ-ence.	De-crease.	Boiling point.	Differ-ence.	De-crease.
Butyl....	77·96	31·48	2·82	99·88	29·06	2·98	129·81	27·63	2·21
Propyl ..	46·48	34·30		70·82	32·04		102·18	29·84	
Ethyl....	12·18			38·78			72·34		

Fatty alcohols.				Fatty acids.			Benzoic ethers.		
	Boiling point.	Difference.	Increase.	Boiling point.	Difference.	Decrease.	Boiling point.	Difference.	Decrease.
Butyl. . .	116·88			162·32			247·32		
Propyl ..	97·41	19·47	0·59	140·66	21·66	0·90	229·47	17·85	0·46
Ethyl. . .	78·53	18·88		118·10	22·56		211·16	18·31	

Acetic ethers.				Propionic ethers.			Butyric ethers.		
	Boiling point.	Difference.	Decrease.	Boiling point.	Difference.	Decrease.	Boiling point.	Difference.	Decrease.
Butyl. . .	124·30			145·99			164·77		
Propyl ..	101·98	22·32	2·66	122·44	23·55	0·09	143·42	21·35	1·01
Ethyl. . .	77·00	24·98		98·82	23·64		121·07	22·35	

Ethyl ethers.				Propyl ethers.			Butyl ethers.		
	Boiling point.	Difference.	Increase.	Boiling point.	Difference.	Increase.	Boiling point.	Difference.	Decrease.
Butyrate ..	121·06			143·42			164·77		
Propionate	98·80	22·26	0·46	122·44	20·98		145·99	18·78	
Acetate ...	77·00	21·80		101·98	20·46	0·52	124·30	21·69	2·91

Isomeric ethers, C <sub>5</sub> H <sub>10</sub> O <sub>2</sub> .			Isomeric ethers, C <sub>6</sub> H <sub>12</sub> O <sub>2</sub> .		
	Boiling point.	Difference.		Boiling point.	Difference.
Propyl acetate ....	101·98		Butyl acetate .....	124·30	
Ethyl propionate ..	98·80	3·18	Propyl propionate ....	122·44	1·86
			Ethyl butyrate .....	121·01	1·43

Isomeric ethers, C<sub>7</sub>H<sub>14</sub>O<sub>2</sub>.

	Boiling point.	Difference.
Butyl propionate .....	145·99	
Propyl butyrate .....	143·42	2·57



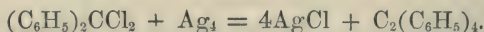
**On the Nomenclature of the Aromatic Compounds.** By  
RUDOLPH FITTIG (Zeitschr. f. Chem. [2], vii, 587).

To do away with the confusion which has arisen in the nomenclature of these compounds, and exclude hypothesis as far as possible, the author suggests the desirability of retaining the prefixes ortho-, meta-, and para-, in preference to the numbers 1 : 2, 1 : 3, 1 : 4, for the purpose of distinguishing the three series of di-substitution products of benzene. The three phthalic acids possessing well-marked characters, the author thinks they would serve as representatives of the three groups, and proposes to regard ordinary phthalic acid as the type of the ortho-compounds, isophthalic acid as the type of the meta-compounds, and terephthalic acid as that of the para-compounds.

W. A. T.

**Derivatives of Tetraphenyl-ethylene.** By A. BEHR (Deut. Chem. Ges. Ber., v, 277).

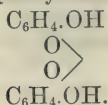
THE hydrocarbon itself is prepared by heating benzophenone chloride with silver—



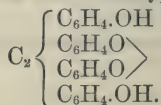
When dissolved in glacial acetic acid and treated with half its weight of chromic acid dissolved in the same menstruum, there is obtained, after boiling until a green colour is observed, a body crystallisable from glacial acetic acid, melting at 193°–194°, and of composition  $C_2(C_6H_5)_4O$ : hence it is termed *tetraphenyl-ethylene oxide*. Further action of chromic acid converts it into benzophenone, melting at 48°.

Concentrated sulphuric acid converts tetraphenyl-ethylene into *tetraphenylethylene-tetrasulphonic acid*, the salts of which are readily soluble in water and not crystallisable. On fusion of the barium salt with three times its weight of caustic potash, *tetraoxyphenyl-ethylene*,  $C_2(C_6H_4OH)_4$  is produced. This substance is crystallisable from acetic acid, and melts above 300°. Ferric chloride in glacial acetic acid solution oxidises it to a crystalline body,  $C_{26}H_{18}O_4 + \frac{1}{2}H_2O$ , the water being lost at 180°, but not at 150°. This substance is a green crystalline powder of metallic lustre. When rubbed in a mortar, the fine powder is red. It is insoluble in water, ether, chloroform, and benzene, sparingly soluble in alcohol. From its composition and mode of formation it is evident that this tetraoxyphenyl-ethylene colouring matter is a quinone derivative.

Quinhydrone.



Colouring matter from tetraoxyphenyl-ethylene.



Alkalis dissolve it with a deep blue-green colour; zinc-dust readily reduces the solution, while alum precipitates a dirty red lake, and acids

throw down the original colouring matter of light or dark red tint, according to the concentration of the liquor.

C. R. A. W.

**On certain Cymene Derivatives.** By F. LANDOLPH (Deut. Chem. Ges. Ber., v, 267).

CYMESE, prepared by the action of phosphorus pentasulphide on camphor, was treated with bromine drop by drop, a little iodine being added, and the whole well cooled. After distillation with water and fractional distillation, *monobromocymene*,  $C_6H_3Br$   $\left\{ \begin{array}{l} CH_3 \\ C_3H_7 \end{array} \right.$ , was obtained as a liquid of weak cymene-like odour, boiling at  $233^\circ$ — $235^\circ$ , and of sp. gr. 1.269 at  $17.5^\circ$ . The bromine in this body is retained with great force, as sodium and methyl iodide, as well as sodium and carbon dioxide, fail to cause its elimination. This appears to be connected with the *position* of the bromine-atom in the molecule, haloïd atoms occupying the *para* place being readily replaceable, but only with difficulty, or not at all, when occupying either of the other positions.

Diluted nitric acid (1 to 4 parts water) readily oxidises bromocymene to *bromotoluic acid*,  $C_6H_3Br$   $\left\{ \begin{array}{l} CH_3 \\ CO.OH \end{array} \right.$ , melting at  $203^\circ$ — $204^\circ$ , difficultly soluble in cold water, but readily in hot water, hot diluted alcohol, ether, and chloroform. It volatilises with water-vapour, and distils unchanged. Sodium amalgam forms ordinary toluic acid, melting at  $176^\circ$ . Neither by nitric acid nor by sulphuric acid and potassium dichromate could a bibasic acid be obtained.

The calcium salt  $Ca(C_8H_6BrO_2)_2 + 3\frac{1}{2}H_2O$ , and the barium salt  $Ba(C_8H_6BrO_2)_2 + 4H_2O$  are crystallisable from hot water, but only sparingly soluble in cold water. Concentrated nitric acid produces *bromonitrotoluic acid*,  $C_6H_2(NO_2)Br$   $\left\{ \begin{array}{l} CH_3 \\ COOH \end{array} \right.$ , on long digestion with bromotoluic acid. This is not volatile with water vapour, and dissolves with difficulty in cold water, but more easily in hot water, alcohol, and ether. Its barium salt is  $Ba(C_8H_5.NO_2.BrO_2)_2 + H_2O$ , and it melts with incipient decomposition between  $170^\circ$  and  $180^\circ$ .

The author mentions that commercial xylene sometimes consists of nearly pure xylene (*para*, giving terephthalic acid by oxidation), sometimes of nearly pure isoxylene (*meta*, giving isophthalic acid). The latter variety had been purified by the sulpho-acid process, which hence perhaps may serve as a means of separation.

The higher-boiling products from camphor and phosphorus pentasulphide are of a phenolic character; while zinc chloride forms laurene,  $C_{11}H_{16}$  (Fittig, Köbrich, and Jilke).

C. R. A. W.

**On Isomeric Amyl Nitrites. Preliminary Communication.**

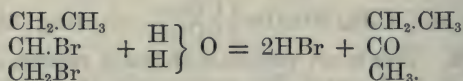
By V. MEYER and O. STÜBER (Deut. Chem. Ges. Ber., v, 203).

IN the expectation that two isomerides can exist, denoted in the ethyl series by the formulæ  $\text{N}=\text{O}$   
 $\text{—O—C}_2\text{H}_5$  and  $\text{N}=\text{O}_2$   
 $\text{—C}_2\text{H}_5$ , silver nitrite (prepared by precipitation) was mixed with the equivalent quantity of amyl iodide, whereby an action took place which was finally completed by heating in an oil-bath with an inverted condenser attached. On fractional distillation of the product, the greater portion distilled at  $150^\circ\text{—}160^\circ$ . Fractions boiling at  $148^\circ\text{—}153^\circ$ ,  $152^\circ\text{—}156^\circ$ ,  $156^\circ\text{—}160^\circ$  gave numbers agreeing with the formula  $\text{C}_5\text{H}_{11}\text{NO}_2$ , whence it appears that the product is isomeric with amyl nitrite, which boils at  $95^\circ$ . Iron and acetic acid acted energetically on the substance, the product giving off the smell of ammonia bases on addition of potash. Aqueous caustic potash in sealed tubes at  $100^\circ$  gave a product from which sulphuric acid precipitated a yellow heavy oil soluble in potash, nitrite being also formed. Not more than  $\frac{1}{46}$  of the crude product distilled between  $80^\circ$  and  $100^\circ$ ; a small quantity distilled above  $160^\circ$ .

C. R. A. W.

**Conversion of Normal Butyl Alcohol into Butylene Hydrate, or Ethylmethyl Carbinol.** By E. LINNEMANN (Ann. Chem. Pharm., clxii, 1).

SAYTZEFF has already performed this conversion by uniting  $\alpha$ -butylene with hydriodic acid, whereby the iodide of ethyl-methyl carbinol is produced (*J. pr. Chem.* [2], 3, 88). By treating brominated normal butyl bromide (identical with normal butylene dibromide) with 20 times its volume of water for 24 hours at  $150^\circ$ , a ketone is formed boiling between  $75^\circ$  and  $80^\circ$ ; this is doubtless ethyl-methyl ketone formed by the reaction—



just as propylene dibromide, under similar conditions, forms dimethyl ketone. By the hydrogenation of ethyl-methyl ketone, ethyl-methyl carbinol will doubtless be produced.

C. R. A. W.

**Conversion of Normal Butyl Alcohol into Isobutyl Alcohol, or Fermentation Butyl Alcohol.** By E. LINNEMANN and V. V. ZOTTA (Ann. Chem. Pharm. clxii, 3).

THIS conversion is in principle the same as that whereby normal propylamine is converted into isopropyl alcohol (*Ann. Chem.* clxi, 43; this Journal [2], 10, 236). The normal amine employed was obtained by hydrogenizing butyronitrile prepared by distilling with dry zinc chloride the ammonium butyrate obtained by passing dry ammonia gas into pure



butyric acid; the pure butyronitrile boiled at  $115^{\circ}$ — $117^{\circ}$  at 744 mm., only this fraction being employed. By mixing this with hydrochloric and sulphuric acid, and allowing the mixture to flow on to zinc, a small quantity of normal butylamine is formed; the unaltered nitrile is distilled off, and the process repeated twenty to twenty-five times. The pure amine has the sp. gr. 0.740 at  $20^{\circ}$ , and boils at  $76^{\circ}$ — $77^{\circ}$ ; it is soluble in all proportions of water, evolving heat. The hydrochloride is very soluble in alcohol, melts at  $195^{\circ}$ , distils with considerable decomposition, and furnishes a platinum salt crystallisable from hot water.

13 grams of butylamine hydrochloride, 22 of silver nitrite, and 500 c.c. water, heated together, furnish ultimately 6 grams of alcohol, of which the principal portion boils between  $105^{\circ}$  and  $110^{\circ}$ ; this is soluble in 8 to 9 parts of water at  $22^{\circ}$ , furnishes a butyric acid on oxidation with potassium dichromate and sulphuric acid, and yields an iodide boiling principally between  $119^{\circ}$  and  $121^{\circ}$ : hence the alcohol is isobutyl alcohol.

C. R. A. W.

### Reduction of Isobutyric Acid to Isobutyl Alcohol.

By E. LINNEMANN and V. v. ZOTTA (Ann. Chem. Pharm., clxii, 7).

THE acid employed for this reaction was prepared by oxidizing fermentation butyl alcohol with solution of pure recrystallised chromic acid mixed with sulphuric acid; the action taking place in well-secured champagne bottles in the water-bath. The acid finally obtained by passing dry hydrochloric acid gas over the anhydrous calcium salt had the corrected boiling point  $154.11^{\circ}$ , and the sp. gr. 0.9503 at  $20^{\circ}$ ; at  $20^{\circ}$  it required 5 parts of water for solution. The calcium salt required 4.5 parts of water for solution at  $18^{\circ}$ , and after drying at  $100^{\circ}$  had the composition  $3(C_4H_7CaO_2) + H_2O(Ca = 20)$ . By distillation of this with calcium formate, isobutyric aldehyde was obtained, having the sp. gr. 0.803 at  $20^{\circ}$ , and a corrected boiling point of  $60^{\circ}$ — $62^{\circ}$ ; it required 9 vols. of water for its solution at  $20^{\circ}$ , and gave crystals with sodium-hydrogen sulphite, potash again separating the aldehyde without alteration; on treatment with water and 5 per cent. sodium amalgam, isobutyl alcohol (boiling at  $106^{\circ}$ — $107^{\circ}$  after dehydration with caustic baryta) was obtained; this had the sp. gr. 0.8025 at  $19^{\circ}$ , dissolved in 9 parts of water at  $18^{\circ}$ , and furnished an iodide boiling at  $118^{\circ}$ — $119^{\circ}$  at 734 mm.; oxidation with chromic acid produced first the smell of butyric aldehyde, and later that of butyric acid.

C. R. A. W.

### Conversion of Isobutyl Alcohol into Trimethyl-carbinol.

By E. LINNEMANN (Ann. Chem. Pharm., clxii, 12).

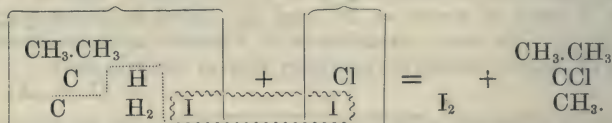
ISOBUTYL iodide of corrected boiling point  $120.6^{\circ}$ , prepared from fermentation alcohol, was treated with thoroughly dry silver acetate for four hours in the water-bath, and then for half an hour in an oil-bath to  $120^{\circ}$ — $125^{\circ}$ ; an ether was thus obtained which boiled at  $113^{\circ}$ — $115^{\circ}$  at 736 mm. On heating with concentrated potash solution in sealed

tubes, this ether furnished an alcohol distilling principally at  $107^{\circ}$  after dehydration by caustic baryta, and yielding a butyric acid on oxidation: hence the iodide employed was the isobutyl iodide, and (as Wurtz has shown previously) furnished the acetic ether of isobutyl alcohol with dry silver acetate. If, however, a mixture of glacial acetic acid and silver acetate be employed, an ether is obtained from which a mixture of alcohols is produced by saponification; the principal part of the alcohol thus obtained boiled between  $80^{\circ}$  and  $85^{\circ}$ , and solidified in a freezing mixture, melting again at  $+4^{\circ}$ : hence isopropyl-carbinol was formed in some quantity.

A mixture of freshly-precipitated silver oxide or mercury oxide, and glacial acetic acid, acted on isobutyl iodide at ordinary temperatures, producing both the acetate of trimethyl-carbinol and trimethyl-carbinol itself, with gaseous butylene and a small quantity of gases not absorbable by bromine; the butylene thus produced furnished a dibromide of corrected boiling point  $149.7^{\circ}$ : hence it was isobutylene. From this butylene a further quantity of trimethyl-carbinol could be obtained by Butlerow's process (*Zeitschr. f. Chem.*, 1870, 237): hence this method of preparing trimethyl-carbinol and its compounds is the most productive known, 38 grams of this alcohol being obtainable ( $27\frac{1}{2}$  as such, about 11 in the form of dibromide = 42 grams) from 100 of isobutyl iodide, 40 grams being the theoretical yield. Butlerow's process yields only 20 grams. A small quantity of isobutyl alcohol is simultaneously obtained.

Isobutyl bromide (from fermentation alcohol by gaseous hydrobromic acid; corrected boiling point  $92.33^{\circ}$ ; sp. gr. 1.2038 at  $16^{\circ}$ ) also furnished trimethyl-carbinol acetate on treatment with mercury oxide and glacial acetic acid; but silver-oxide had no action. Similarly isobutyl chloride (from fermentation alcohol and gaseous hydrochloric acid; boiling point  $67^{\circ}$ — $69^{\circ}$ ; corrected  $68.5^{\circ}$ ; sp. gr. 0.8798 at  $15^{\circ}$ ) was scarcely acted on by either mercury or silver oxide, together with glacial acetic acid.

Iodine monochloride acts on isobutyl iodide just as on propyl iodide, so far as the conversion of iodide into chloride is concerned; but whereas in the propyl series the normal iodide yields the normal chloride (this *Journal* [2], 10, 235); isobutyl iodide forms the chloride corresponding to trimethyl-carbinol—



The chloride thus produced boiled almost wholly at  $46^{\circ}$ — $52^{\circ}$ , and, on treatment with water for several hours at  $100^{\circ}$ , was almost perfectly converted into trimethyl-carbinol, boiling wholly below  $82^{\circ}$  after dehydration by caustic baryta, soluble in water in all proportions, and crystallising in a freezing mixture, the crystals melting at  $+15^{\circ}$ .

Isobutyl iodide, heated with dry silver cyanate, forms a dry, solid compound of silver iodide and butyl cyanate; this, mixed with finely-



divided caustic potash and heated in small portions at a time, gives off vapours of the amine, *not* of isobutyl alcohol, but of trimethyl-carbinol; these are absorbed by hydrochloric acid, and the hydrochloride formed separated from ammonium chloride by alcohol after evaporation to dryness: pure *trimethyl-carbinolamine* boils at  $45^{\circ}$ — $46^{\circ}$ , and has the sp. gr. 0.6987 at  $15^{\circ}$ . A constant difference of about  $53^{\circ}$  is thus perceptible between the boiling points of the iodides and amines of alcohol-radicals; thus—

	Iodide.	Amine.	Difference.
Ethyl.....	72	18.7	53.3
Propyl .....	102.2	49	53.2
Butyl.....	129.9	76.5	53.4
Isobutyl.....	120.6	67.5	53.1
Trimethyl-carbinol .....	98.5	46	52.5

Trimethyl-carbinolamine hydrochloride melts above  $250^{\circ}$ , and is capable of being distilled; it is soluble in 1.7 parts of water at  $15^{\circ}$ ; it forms a platinum salt, soluble to some extent in alcohol; nitrite of silver produces trimethyl-carbinol, boiling between  $80.5^{\circ}$  and  $83^{\circ}$ , and solid at  $+16^{\circ}$ .

Isobutylamine (prepared from isobutyl-potassium sulphate and potassium cyanate and treatment of the product with caustic potash) also yields trimethyl-carbinol on treatment of its hydrochloride with silver nitrite; after dehydration by caustic baryta, the alcohol boils at  $81^{\circ}$ — $85^{\circ}$ , and becomes solid in a freezing mixture, melting at  $+2^{\circ}$ . The isobutylamine itself boils at  $65.8^{\circ}$ — $68.3^{\circ}$  at 743 mm., has the sp. gr. 0.7357 at  $15^{\circ}$ , is soluble in all proportions of water, and becomes solid by exposure to air, forming a carbonate; its hydrochloride dissolves in 0.73 parts of water at  $15^{\circ}$ , and melts at  $160^{\circ}$ ; its platinum salt is sparingly soluble in water. The action of nitrous acid on monamines may thus be described as always producing the *alcohol of a radical containing one more methyl group than the original amine* (provided the amine be capable of forming an isomeride containing one more methyl group): thus normal propylamine gives isopropyl alcohol; normal butylamine, isobutyl alcohol; and isobutylamine, trimethyl-carbinol.

Pure trimethyl-carbinol is a colourless liquid of peculiar odour, soluble in water in all proportions; its sp. gr. is 0.7792 at  $37^{\circ}$ , and its corrected boiling point  $82.94^{\circ}$ ; when pure it solidifies readily below  $20^{\circ}$ , frequently remaining liquid, however, till a fragment of platinum gauze is thrown in; it melts below  $23^{\circ}$  and  $24^{\circ}$ ; Butlerow's method of dehydrating it by calcium chloride is not to be recommended, as the anhydrous salt partially etherifies it, a compound being formed which is only decomposed at  $150^{\circ}$  to  $200^{\circ}$ : if the chloride contain so much water that the alcohol can be distilled off in the water-bath, the alcohol which distils contains as much water as at first: repeated treatment with caustic baryta in sealed tubes in the water-bath completely dehydrates it.

The formation of trimethyl-carbinol from isobutyl iodide by means of silver oxide and glacial acetic acid may be explained by supposing that the elements of hydriodic acid are first removed, forming isobuty-



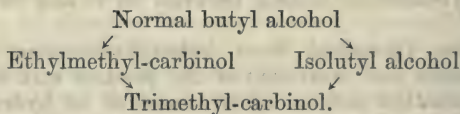
lene, which in the nascent state combines with the elements of acetic acid, forming the acetate of trimethyl-carbinol; the simultaneous formation of this acid, trimethyl-carbinol itself, and isobutylene, is in favour of this view: the numerous cases of isomeric variation of a radical above described, indicate that it is not possible to conclude with certainty what may be the structural formula of a generating substance by the examination of its products; these isomeric variations being of this character, that the groups affected are so altered as to produce an additional methyl group in place of one of the groups so changed.

C. R. A. W.

### Inverse Formation (Rückbildung) in the Tetryl Series.

By E. LINNEMANN (Ann. Chem. Pharm., clxii, 30).

THE author's former papers have shown that from normal butyl alcohol there may be produced either butylene hydrate (ethyl-methyl-carbinol) or isobutyl alcohol; and that either of these two can be converted into trimethyl-carbinol, so that the four alcohols stand to one another in the relation—



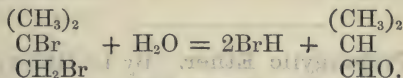
Reactions whereby the direction of derivatives can be reversed (*i.e.*, isobutyl alcohol from trimethyl-carbinol, or normal butyl alcohol from ethylmethyl-carbinol) are desiderata: probably by hydrogenising either normal butyl iodide or ethylmethyl-carbinol iodide, the normal hydrocarbon will result, identical with diethyl, from which Schöyen has, apparently, obtained normal butyl chloride (*Ann. Chem. Pharm.*, cxxx, 233); similarly, by hydrogenising either of the iodides of the other two alcohols, the hydrocarbon trimethyl-methane,  $\text{CH}(\text{CH}_3)_3$ , will result, from which probably isobutyl derivatives will be obtained by the action of chlorine or bromine: the latter is perhaps preferable to chlorine for Schorlemmer's reactions in the case of the more volatile hydrocarbons, such as butyl and amyl hydrides.

C. R. A. W.

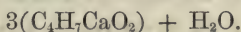
### Inverse Formation of Isobutyl Alcohol from Trimethyl-carbinol. By E. LINNEMANN and V. VON ZOTTA (*Ann. Chem. Pharm.*, clxii, 33).

BUTLEROW has performed this conversion by combining butylene from trimethyl-carbinol with hypochlorous acid, whereby a chlorhydrin is produced which yields isobutyl alcohol on treatment with sodium amalgam. The dibromide of this butylene is identical with monobrominated trimethyl-carbinol bromide, and with the dibromide of the butylene from isobutyl alcohol; the authors find that this dibromide is also produced by acting on isobutyl iodide with bromine, not in excess; the product boiling at  $146^\circ$ — $150^\circ$  (isobutyl bromide similarly treated

does not, however, form this product, but produces dibrominated isobutyl bromide, boiling at  $214^{\circ}$ — $218^{\circ}$ ). On treating this dibromide with 20 volumes of water at  $150^{\circ}$ — $160^{\circ}$  for 24 hours, isobutyric aldehyde is formed, thus—



This reaction is observed with the dibromide from isobutyl iodide, also with that from the combination of pure isobutylene (from pure isobutyl alcohol) with bromine; by oxidation with silver oxide the aldehyde furnished isobutyric acid, recognized by the analysis of its silver and calcium salts: the latter required 4.03 parts of water at  $18^{\circ}$  for solution, and, after drying at  $100^{\circ}$ , had the composition—



It has been previously shown that this aldehyde furnishes isobutyl alcohol by hydrogenation: hence another means is afforded of passing from trimethyl-carbinol to isobutyl alcohols.

C. R. A. W.

#### Researches on the Derivatives of Glycerin. Part IV. Glycide Compounds. By L. HENRY (Deut. Chem. Ges. Ber., v, 186—192).

EPIDICHLORHYDRIN and epidibromhydrin must be regarded as substitution-products of allyl chloride and bromide. On acting upon them with potassium acetate, the acetic ethers of monochlor- and monobromallyl are formed, and by using potassium sulphocyanate the corresponding sulphocyanic ethers are readily obtained.

*Monochlorallyl sulphocyanate*,  $(\text{C}_3\text{H}_4\text{Cl})\text{SCN}$ , is a colourless liquid boiling at  $185^{\circ}$ , and possessing a very pungent smell, like that of mustard-oil. It combines quickly with ammonia, yielding *monochlorothiosinnamine*,  $\text{CS} \left\{ \begin{array}{l} \text{NH}_2 \\ \text{NH.C}_3\text{H}_4\text{Cl} \end{array} \right\}$  in colourless crystals, melting at  $90^{\circ}$ — $91^{\circ}$ . Monobromallyl sulphocyanate boils at  $200^{\circ}$  and yields a thiosinnamin melting at  $110^{\circ}$ — $111^{\circ}$ .

*Monobromallyl-ethyl ether*,  $\text{C}_3\text{H}_4\text{BrOC}_2\text{H}_5$ , is obtained by distilling ethoxydibromhydrin,  $\text{C}_3\text{H}_5\text{Br}_2\text{OC}_2\text{H}_5$ , with caustic soda. It is a colourless liquid having a pleasant smell, and boiling at  $130^{\circ}$ — $135^{\circ}$ . It is easily transformed into propargylether,  $\text{C}_3\text{H}_3\text{OC}_2\text{H}_5$ , by heating it with an alcoholic potash-solution.

*Monochlorallyl-ethyl ether*,  $\text{C}_3\text{H}_4\text{ClOC}_2\text{H}_5$ , is formed by the action of alkalis upon ethoxybichlorhydrin; it boils at  $120^{\circ}$ .

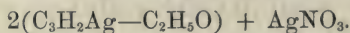
The formation of these substituted allyl compounds is quite analogous to that of monochlorpropylene from propylene dichloride. They contain, therefore, the chlorine or bromine combined with the middle carbon atom of the allyl group. This is further proved by the fact, that by the action of sulphuric acid upon pure epidichlorhydrin, monochloracetone is formed, whilst, as Oppenheim has shown, acetone is obtained by acting with sulphuric acid upon monochlorpropylene.

Epidibromhydrin does not boil at  $151^{\circ}$ — $152^{\circ}$ , as Reboul has stated, but at about  $10^{\circ}$  lower; it appears to be identical with the compound boiling at the same temperature which Tollens obtained by acting with sodium upon tribromhydrin.

C. S.

**Preparation of Propargylic Ether.** By L. HENRY (Deut. Chem. Ges. Ber., v, 274).

WHEN monobromallylic ether is heated with its own weight of caustic potash dissolved in as little alcohol as possible, an inverted condenser being attached, it loses the elements of hydrobromic acid, and produces almost the theoretical quantity of propargylic ether; most of this separates as an oil on dilution with water, the remainder being obtained, on addition of silver nitrate to the aqueous distillate, as a crystalline body,



It is very difficult to separate the last traces of alcohol and moisture from the ether, treatment with sodium amalgam being requisite; when thus dried it boils at  $81^{\circ}$ — $85^{\circ}$ , and has the sp. gr. 0.83 at  $7^{\circ}$ : sodium produces a white solid substance,  $(\text{C}_3\text{H}_2\text{Na})\text{C}_2\text{H}_5\text{O}$ ; further researches to see if this body will combine with  $\text{CO}_2$  (as the sodium compound of acetylenyl-benzene,  $\text{C}_6\text{H}_5\cdot\text{C}_2\text{Na}$ , does with the production of phenylpropionic acid,  $\text{C}_6\text{H}_5\cdot\text{C}_2\cdot\text{CO}\cdot\text{OH}$ ), and to elucidate other points, are promised.

C. R. A. W.

**On Sorbite, a Saccharine Matter analogous to Mannite, found in the Juice of Mountain-ash Berries.** By J. BOUSSINGAULT (Compt. rend., lxxiv, 939—942).

MOUNTAIN-ash berries, like cherries, plums, apples, &c., do not yield alcohol in proportion to the amount of saccharine matter which they contain. In a quantity of juice from these berries, containing 372.96 grams of saccharine matter, and fermented under favourable conditions, only 296.17 grams were decomposed, and the quantity of alcohol produced was but 135.09 grams, instead of 151.37 grams required by calculation.

The liquid containing the undecomposed saccharine matter yielded a crystalline substance, having, when dried at  $110^{\circ}$ , the composition,  $\text{C}_6\text{H}_{14}\text{O}_6$ , and to which the author has given the name of *sorbite*.\* It is isomeric with mannite and dulcitate, but in the form of its crystals, in its melting point and other properties, it differs greatly from both those substances. Sorbite separates from aqueous solution in crystals containing  $2\text{C}_6\text{H}_{14}\text{O}_6\cdot\text{H}_2\text{O}$ , which melt at  $102^{\circ}$ . The anhydrous substance melts at  $110^{\circ}$ — $111^{\circ}$ , whereas mannite melts at  $165^{\circ}$ , and dulcitate at  $182^{\circ}$ . Sorbite is not a product of fermentation, as it can be obtained from the juice immediately after expression.

J. B.

\* Pelouze, in 1852 (*Ann. Chim. Phys.* [3], xxxv, 292), obtained from mountain-ash berries, a crystallisable, non-fermentable sugar, called *sorbin*, having the composition of glucose.—ED.



**On Some Metallic Trichloracetates.** By A. CLERMONT (Compt. rend., lxxiv, 942—944).

THE author, in continuing his experiments already reported, has analysed the following salts:—

Acid Potassium Trichloracetate....	$C_2Cl_3KO_2$	$C_2Cl_3HO_2$ .
Lithium Trichloracetate .....	$C_2Cl_3LiO_2$	$.2H_2O$ .
Magnesium Trichloracetate.....	$C_2Cl_3Mg'O_2$	$.2H_2O$ .
Nickel Trichloracetate.....	$C_2Cl_3NiO_2$	$.2H_2O$ .

These bodies crystallise out from a solution obtained by dissolving the respective carbonates in trichloroacetic acid. The magnesium and lithium salts require several months for crystallisation; the crystals of both are deliquescent, and those of the latter can only be kept in sealed tubes. All the preceding salts agree in composition with their corresponding acetates, and the introduction of chlorine has therefore left the type of their formation unaltered.

J. B.

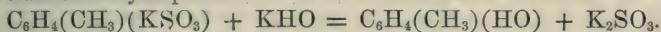
**Formation of Phenols from Aromatic Hydrocarbons.** By A.D. WURTZ (Ann. Chim. Phys. [4], xxv, 108).

THE sulphonic acids of benzene, toluene, and naphthalene, when decomposed by melting potash in the same manner as ethyl-sulphurous acid, yielding a sulphite and an alcohol. In this manner benzene may be converted into phenol, toluene into cresol, &c.

Toluene from coal-tar, boiling at  $110^\circ$ , was converted into toluyl-sulphurous acid, and the latter decomposed by alkali as above.

Potassium toluylsulphite.

Cresol.



The resulting cresol, however, separates at a low temperature into two isomeric cresols, one solid and the other liquid, arising from the simultaneous formation by the action of sulphuric acid of two isomeric sulpho-conjugated acids. By the further action of potash, the liquid cresol yields salicylic acid, the solid cresol, paroxybenzoic acid, which are removed by agitation with aqueous ammonium carbonate. The mixed product is then fractionally distilled. The portion boiling above  $198^\circ$ , on exposure to a cold below  $0^\circ$ , gives colourless crystals of the solid cresol, purifiable by pressure and washing with ether. It melts at  $34.5^\circ$ , boils at  $202^\circ$ , and contains 77.36 per cent. of carbon, and 7.53 hydrogen. The remaining portions consist mainly of the liquid cresol.

*Xylene into Xylenols.*—Xylene from coal-tar, boiling at  $139^\circ$  (composed chiefly of meta- or isoxylene) is shaken with twice its volume of ordinary sulphuric acid, warmed, diluted, saturated with barium carbonate, the filtered solution decomposed exactly with potassium carbonate, the filtrate evaporated, and the dry salt fused with potash. The solid and liquid xylenols are separated by freezing and pressure.

*Solid Xylenol* crystallises from ether in brilliant colourless plates, assuming a pearly lustre by pressure, and abundantly soluble in alcohol and ether. They melt at  $75^{\circ}$ , and boil at  $213.5^{\circ}$ . Melted xylene has a density of 0.9709 at  $81^{\circ}$ ; it emits copious vapours, condensing in light very brilliant crystals, with an odour resembling phenol; on cooling, it solidifies to a white crystalline mass, with a contraction, between  $81^{\circ}$  and  $69^{\circ}$ , of more than a tenth of its volume.

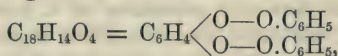
*Liquid Xylenol* is a colourless, highly refracting fluid, smelling strongly of phenol: density, 1.036 at  $0^{\circ}$ , 0.9700 at  $81^{\circ}$ , its co-efficient of expansion between these temperatures being 0.000868. Boiling point  $211.5^{\circ}$ . It is soluble in all proportions in alcohol and ether. It dissolves in small quantity in water, and can itself dissolve a trace of that liquid. As the xylene, however, contains in solution a little of the solid modification, its physical properties are given with a certain reserve. The analysis of both the isomerides leads to the formula  $C_8H_{10}O$ . Their isomerism arises from the different positions in the nucleus of the radicles,  $CH_3$  and  $HO$ .

The above reactions with the conjugated sulpho-acids are of very general application. The conversion of anthracene into alizarin involves a similar use of sulphuric acid.

C. G. S.

**Oxidation of Phenol.** By H. WICHELHAUS (Deut. Chem. Ges. Ber., v, 248—250).

ON digesting phenol dissolved in water, with two and a-half times its weight of chromic acid for half an hour, chromium oxide separates, and on subjecting the solution to distillation, an aqueous liquid passes over, having a distinctly yellow colour. By agitating this with ether, and evaporating the ethereal solution, a dark red crystalline mass is obtained which, by pressure and subsequent sublimation, yields beautiful red needles, with green metallic lustre, melting at  $71^{\circ}$ . These crystals, to which the author assigns the formula—



dissolve in water, and more readily in alcohol and ether.

The first oxidation-product of phenol is quinone, which combines with unaltered phenol, forming a new compound having the constitution just expressed. This was proved to be the case by adding quinone to a solution of phenol, when the same red compound was obtained; various reduction-products, however, were formed at the same time, amongst which indications of the presence of green quinhydrone were obtained. The new substance, which the author names *phenoquinone*, is not altered by chromic acid in the cold, neither does it form salts. It splits up under the influence of heat, and of various reagents, yielding phenol and quinone, or the products of their decomposition.

C. E. G.

**Dinitrophenols.** By H. HUEBNER and W. SCHNEIDER (Zeitschr. f. Chem. [2], viii, 523—528).

THE authors now give a detailed description of the preparation, salts, &c., of the isomeric dinitrophenols obtained by nitration of volatile mononitrophenol (this Journal, vol. x, 241).

20—25 grams of mononitrophenol and the same weight of nitric acid (sp. gr. 1.37) are gently heated together until reaction sets in. The reaction is excessively violent. The product forms two layers: the lower a thick oil, which solidifies after some time only in the cold, is a mixture of much ordinary ( $\alpha$ ) dinitrophenol with the new ( $\beta$ ) dinitrophenol, and more or less trinitrophenol and unaltered nitrophenol. (Nitric acid acts with far less violence on the non-volatile mononitrophenol, forming  $\alpha$ -dinitrophenol only.) The crystalline mass, after being washed with very cold water to remove adhering nitric acid, was boiled with water in a flask so long as volatile mononitrophenol distilled over, and finally converted into barium salts and fractionally crystallised. Barium  $\alpha$ -dinitrophenate is readily soluble in water of 30°—40°, whereas the  $\beta$ -barium salt is but very slightly soluble in water at the same temperature. The behaviour of these two salts with alcohol affords even a better method of separation; boiling 90 per cent. alcohol dissolves the  $\alpha$ -salt with moderate readiness, but takes up traces only of the  $\beta$ -salt.

$\alpha$ -Dinitrophenol crystallises from water in yellowish white, fern-like plates. It melts at 113°—114°, but does not melt under water. It is slightly soluble in cold, more soluble in hot water; easily soluble in benzene, chloroform, and ether, but to a less extent than  $\beta$ -dinitrophenol; it is more volatile in a current of steam than the latter.  $\alpha$ -Dinitrophenol is especially characterised by a tendency to form salts crystallising with varying amounts of water.

$\beta$ -Dinitrophenol crystallises from water in fine, short needles, pointed at either end, which melt at 64° and fuse to an oil under water. It is more soluble than the  $\alpha$ -phenol in cold water, less soluble than it is in boiling water. The potassium, sodium, and magnesium salts of this phenol are highly characteristic and distinguishes it sharply from the  $\alpha$ -compound.

The following salts were obtained:—

$\alpha$ -Series from volatile and non-volatile nitrophenol.	$\beta$ -Series from volatile nitrophenol.
<p>(a) <math>(C_6H_3(NO_2)_2O)_2Ba + 7aq.</math> Prismatic, golden-yellow needles.</p> <p>(b) <math>(C_6H_3(NO_2)_2O)_2Ba + 6aq.</math> Fine pale-yellow needles.</p> <p>(c) <math>(C_6H_3(NO_2)_2O)_2Ba + 5aq.</math> Orange-red prisms.</p>	<p><math>(C_6H_3(NO_2)_2O)_2Ba + aq.</math> Flat golden-yellow striated needles.</p>
<p>(a) <math>C_6H_3(NO_2)_2OK + aq.</math> Dark yellow prisms.</p> <p>(b) <math>C_6H_3(NO_2)_2OK + \frac{1}{2}aq.</math> Pale-yellow six-sided needles.</p>	<p><math>C_6H_3(NO_2)_2OK.</math> Flat, red, trichroic needles.</p>



$\alpha$ -Series from volatile and non-volatile nitrophenol.	$\beta$ -Series from volatile nitrophenol.
$C_6H_3(NO_2)_2ONa$ + aq. Fine small yellow needles.	$C_6H_3(NO_2)_2ONa$ + 3aq. Long, bright red needles.
(a) $(C_6H_3(NO_2)_2O)_2Mg$ + 12aq. Pale yellow thick prisms. (b) $(C_6H_3(NO_2)_2O)_2Mg$ + 9aq. Pale-yellow prismatic needles.	$(C_6H_3(NO_2)_2O)_2Mg$ + 6aq. Glistening, bright-red needles.
$(C_6H_3(NO_2)_2OPb)_2$ + 6aq. Long, golden yellow needles.	$(C_6H_3(NO_2)_2OPb)_2$ . Yellow-red fine needles.

L. Henking finds that both  $\alpha$ - and  $\beta$ -dinitrophenol yield the same trinitrophenol (melting point  $120^\circ$ ) on further nitration.

H. E. A.

### Direct Oxidation of Anthraquinone by Potassium Hydrate.

By V. WARTHA (*Ann. Chem. Pharm.*, clxi, 305).

GRAEBE and LIEBERMANN (*Ann. Chem. Pharm.*, clx, 129) did not succeed in isolating alizarin from the product of the action of fused potash on anthraquinone, although they found the latter to be altered.

The author, who had previously stated that alizarin was produced (*Deut. Chem. Ges. Ber.*, 1870, 545) by this reaction, has repeated and confirmed his former experiments. He finds that if anthraquinone be heated with aqueous potash, an alcoholic solution of anthraquinone then added, and the heating continued, the fused mass being continuously stirred, at first a green colour is observed, which finally passes into the purple-blue of potassium-alizarin. On the addition of hydrochloric acid to the solution of the fused mass, alizarin is precipitated and may be extracted by ether. The quantity obtained is, however, very small. It is also necessary to employ an alcoholic solution of anthraquinone, or to mix some potassium or sodium ethylate with the latter before adding it to the fused potash.

H. E. A.

### Electrolysis of the substituted Derivatives of Acetic Acid.

By G. E. MOORE (*Amer. J. Sci.* [3], iii, 177—179).

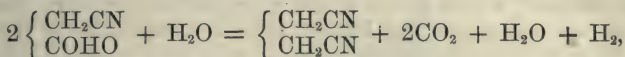
It is well known that by the electrolysis of acetic acid methyl is separated. Arguing from analogy, therefore, we might expect, by the electrolysis of the chloro- or cyano-derivatives of acetic acid, to effect the separation of the substituted radical. The decomposition may be formulated thus:—



The results obtained by the electrolysis of monocyanacetic acid were in the first instance purely negative, no substance answering to the

characters of monocyanmethyl being capable of separation from among the products of the decomposition. But, upon a more careful investigation of the contents of the positive cell, a deliquescent acid substance was separated by means of ether, which appeared to agree in its physical and other characteristics with ethylene cyanide.

It was solid at ordinary temperatures and melted at  $37.8^{\circ}$ . When boiled with caustic potash-solution, it evolved ammonia, leaving a residue, which, by means of its suffocating vapour and reaction with ferric chloride, was recognized as ethylene-succinic acid. The course of this phase of the decomposition may therefore be represented in the following manner:—



a reaction precisely analogous to that which is in fact generally supposed to occur during the electrolysis of potassium acetate, in which *dimethyl* is obtained.

The author purposes to extend the investigation to the second and third substitution-compounds of acetic acid.

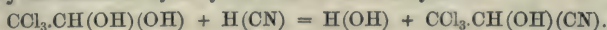
J. W.

**Trichlorolactic and Trichlorangelactic Acids.** By C. BISCHOFF and A. PINNER (Deut. Chem. Ges. Ber. v, 208).

CHLORAL and aqueous hydrocyanic acid were digested in a vessel with attached condenser; finally the product was evaporated to dryness on the water-bath; an oily product, solidifying to a mass of crystals, was obtained, having the composition  $\text{CCl}_3 - \text{CH} \left\{ \begin{array}{l} \text{OH} \\ \text{CN} \end{array} \right.$ , and therefore produced by direct addition of hydrocyanic acid to chloral.\* Long continued boiling with hydrochloric acid converted this cyanhydrin into *trichlorolactic acid*,  $\text{CCl}_3 - \text{CH} \left\{ \begin{array}{l} \text{OH} \\ \text{CO.OH} \end{array} \right.$ , melting at  $105^{\circ}$ — $110^{\circ}$ . The salts readily split up into chloral and formate on heating with excess of base, the chloral being further decomposed into chloroform and formic acid by strong bases. The ethyl salt was obtained by treatment with alcohol and hydrogen chloride; it was crystallisable, melting at  $66^{\circ}$ — $67^{\circ}$ .

On similar treatment, crotonic chloral formed the corresponding cyanhydrin,  $\text{CHCl} = \text{CCl} - \text{CHCl} - \text{CH} \left\{ \begin{array}{l} \text{OH} \\ \text{CN} \end{array} \right.$ , the production being facilitated by addition of alcohol to dissolve the crotonic chloral; the yield equalled the theoretical amount (which was not quite the case with ordinary chloral, owing to the greater volatility of the cyanhydrin formed from it). On long digestion of this compound with strong hydrochloric acid, *trichlorangelactic acid*,  $\text{CHCl} = \text{CCl} - \text{CHCl} - \text{CH} \left\{ \begin{array}{l} \text{OH} \\ \text{CO.OH} \end{array} \right.$ , is

\* Or by the action of hydrocyanic acid on chloral hydrate—



produced; this acid melts at  $140^{\circ}$ . Further experiments to obtain angelic acid, and in continuation, are contemplated.

C. R. A. W.

**Dextronic Acid.** By J. HABERMANN (Deut. Chem. Ges. Ber., v, 167).

DEXTRONIC acid is obtained from dextrin in the same way as lactonic acid from milk sugar, *i.e.*, by bromination and treatment with silver oxide: the crude acid yields a crystallisable calcium salt, and is best purified by precipitating with lead acetate and treatment with sulphuretted hydrogen; it then forms a sour uncrystallisable syrup. Its ordinary salts are monobasic, but bibasic salts are obtainable in the same way as the corresponding salts of gluconic acid, with which it is merely isomeric and not identical. The two acids differ by  $5^{\circ}$  in their molecular rotatory powers, and in their calcium and barium salts.

*Calcium salt.*

Dextronic acid  $C_6H_{11}Ca'O_7 + \frac{1}{2}H_2O$ . Soluble in 34 of water at  $16^{\circ}$ .  
 Gluconic acid  $C_6H_{11}Ca'O_7 + H_2O$  „ 25 „

*Barium salt.*

Dextronic acid  $C_6H_{11}Ba'O_7 + 2H_2O$ . Soluble in  $5\frac{1}{2}$  water at  $30^{\circ}$ .  
 Gluconic acid  $C_6H_{11}Ba'O_7 + 1\frac{1}{2}H_2O$  „ 6 „

C. R. A. W.

**Researches on Sorbic and Parasorbic Acids.** By R. FITTIG and J. B. BARRINGER (Ann. Chem. Pharm., clxi, 307—328).

THIS memoir contains the results of a first series of experiments undertaken with the view of determining the relation of sorbic acid to its supposed isomeride parasorbic acid, and to other known compounds, sorbic acid being one of a series of acids of the general formula  $C_nH_{2n-8}.CO.OH$ .

On distilling pure sorbic acid, it begins to boil at about  $228^{\circ}$ , but decomposition takes place: a yellow resinoid mass remains in the retort, and the acid which passes over is less pure. The odour of acrolein was perceptible during the distillation, which circumstance, together with the perfect resemblance of the residue in the retort to acrolein resin, leads the authors to believe that sorbic acid splits up on distillation into two molecules of acrolein, and that the resinous mass consists of condensation-products of the latter. Sorbic acid may be distilled, apparently unaltered, in a current of steam.

*Hydrosorbic Acid.*—On treatment with sodium amalgam and water, sorbic acid,  $C_6H_8O_2$ , is readily converted into hydrosorbic acid,  $C_6H_{10}O_2$ , a colourless liquid boiling at  $204.5^{\circ}$  (corr.). It has a specific gravity of .969 at  $19^{\circ}$ , and is still liquid at  $18^{\circ}$ . It is but slightly soluble in water, and volatilises readily in a current of steam. It yields well characterised salts, several of which are described.

*Ethyl Hydrosorbate*,  $C_6H_8O_2.C_2H_5$ , is a colourless liquid, having a



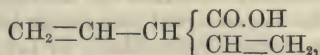
pleasant fruity odour, which boils constantly at  $166^{\circ}$ — $167^{\circ}$ . The continued action of nascent hydrogen produced no alteration of hydrosorbic acid. In the preparation of hydrosorbic acid, a small quantity of an oily bye-product of very high boiling point was obtained; this decomposed on distillation, and gave a barium salt of the same composition as barium hydrosorbate, so that it is probably a polymeric acid.

*Dibromocaproic Acid.*—Bromine acts violently on hydrosorbic acid at ordinary temperatures with evolution of hydrogen bromide, but in the cold the additive compound,  $C_6H_{10}Br_2O_2$  (hydrosorbic dibromide or dibromocaproic acid) is formed. It is a colourless, viscid liquid, insoluble in water. Alcoholic potash reconverts it into sorbic acid, crystallising in long white needles, which melt at  $132^{\circ}$ — $134^{\circ}$ .

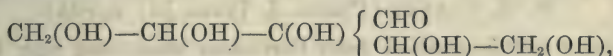
*Behaviour of Hydrosorbic Acid with Potassium Hydrate.*—It is not affected by heating for 10 hours to  $180^{\circ}$  with an excess of potash, but is decomposed on gently fusing the mixture. Butyric acid appears to be the sole product of the reaction. The authors then discuss at some length the value of fusion with potassium hydrate as a means of determining the constitution of acids of the acrylic series; they regard the formula—



for hydrosorbic acid as most in accordance with its behaviour on fusion with potash, whereby the group  $CH=CH_2$  is split off, replaced by hydrogen and oxidised to oxalic, and finally to carbonic acid. To sorbic acid they give the formula—



which explains the probable decomposition into two molecules of acrolein on distillation, and they call attention to the close relationship which this formula exhibits to that previously ascribed by one of the authors (Fittig) to sorbin—



a carbohydrate occurring together with sorbic acid in mountain-ash berries.

*Behaviour of Sorbic Acid with Bromine.*—Numerous attempts to prepare the bromo-compound,  $C_{10}H_8Br_2O_2$ , corresponding to hydrosorbic acid were unsuccessful, but the tetrabromide,  $C_{10}H_8Br_4O_2$ , was readily obtained on triturating sorbic acid with the necessary quantity of bromine under water. A viscous almost colourless mass is formed, which is best purified by taking advantage of the fact that the sodium salt of the tetrabromide is excessively soluble in water, but only slightly soluble in a concentrated solution of sodium carbonate. The mass is therefore dissolved in cold solution of sodium carbonate, a concentrated solution of the latter is then added, the crystals which separate are filtered off, and, after washing with sodium carbonate, are dissolved in water; on the addition of hydrochloric acid the tetrabromide falls

down as a brilliant white precipitate. It crystallises from alcohol in large colourless, transparent crystals, probably a combination or a monoclinic prism  $\propto P$  with the pinacoid  $OP$ . It is scarcely soluble in water. Melts at  $183^{\circ}$ . It is a highly stable compound when pure; similarly the pure sodium salt is unaffected by boiling with water or alcohol, but if it retains mere traces of sodium carbonate, it is at once decomposed on heating, hydrochloric acid no longer forming a precipitate in the solution.

*Parasorbic Acid*.—Hofmann's experiments led him to regard parasorbic acid as an isomeride of sorbic acid; but the authors, who have operated on an acid obtained from Marquart of Bonn, which in the main possessed the properties described by Hofmann as characteristic of parasorbic acid, are of the opinion that it is simply impure sorbic acid. Thus when treated with sodium amalgam it gave hydrosorbic acid. Hofmann gives  $221^{\circ}$  as the boiling point of parasorbic acid, which is very near that of sorbic acid determined by the authors; further, he states it to be a liquid, of less pronounced acid properties than sorbic acid, soluble in alkaline carbonates without evolution of carbonic anhydride. The specimen under examination, however, did evolve carbonic anhydride when dissolved in warm sodium carbonate solution, and also when heated in a retort with water and barium carbonate; at the same time a resinous body remained undissolved, and on distillation an indifferent oil passed over, possessing in a high degree the peculiar, obnoxious odour of parasorbic acid. The filtered solution was evaporated and treated with hydrochloric acid, when a crystalline substance was obtained having all the properties of pure sorbic acid.

In conclusion, the authors note that the methods whereby, according to Hofmann, parasorbic is converted into sorbic acid, viz., heating with solid potash, or concentrated hydrochloric or sulphuric acids, are just those most calculated to remove impurities.

H. E. A.

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**Preparation of Chrysammic Acid and Chrysammates.** By  
W. A. TILDEN (Pharm. J. Trans. [3], ii, 845).

THE aloïn which is obtained from Barbadoes aloes, and may be aptly termed "barbaloin," is perhaps the most abundant source of aloetic and chrysammic acids. It is prepared by dissolving the aloes in boiling water slightly acidulated with hydrochloric acid, and evaporating the filtered liquor until it has acquired a syrupy consistence; in a few days a lemon-yellow mass of barbaloin results, which, after having been partially purified by draining and pressure, may be used directly for the preparation of chrysammic acid.

By the action of cold fuming nitric acid, the aloïn is converted into a mixture of aloetic, chrysammic, oxalic, and picric acids, of which the two former are but very slightly soluble in cold water, and advantage is taken of this circumstance to remove the oxalic and picric acids.

The aloetic acid is finally converted into chrysammic acid by protracted boiling with nitric acid, and the crystalline precipitate of chrysammic acid purified by washing with water, and converting it into, and recrystallising the potassium salt.

Barbaloin yields in this manner more than one-third of its weight of pure potassium chrysammate.

The acid is obtained by dissolving potassium chrysammate in boiling water, and strongly acidifying the liquid with acetic acid. It crystallises in thin yellow fern-shaped crystals, somewhat resembling picric acid, but more lustrous.

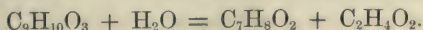
*Lead and Barium Chrysammates.*—These salts have been described by Schunck and Mulder as red powders, the former containing variable proportions of lead. They may, however, be obtained in a crystalline and perfectly definite condition by mixing a solution of the potassium salt with solution of lead or barium acetate, acidified with acetic acid. The crystals of the lead salt exhibit a magnificent bronze reflection and strongly polarize transmitted light.

Analysis assigned to them the formulæ  $C_{14}H_2Pb''(NO_2)_4O_4.4H_2O$  and  $C_{14}H_2Ba''(NO_2)_4O_4.2H_2O$ . If chrysammic acid be correctly represented as a derivative of anthraquinone, it must undoubtedly possess bibasic properties; the author has, therefore, endeavoured to prepare some salts the constitution of which might help to decide this question. At present he has not been successful in producing acid or double salts presenting such characters as would entitle them to be considered definite compounds.

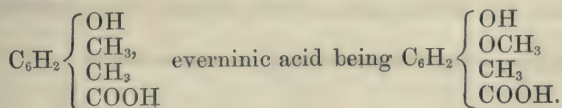
J. W.

**New Acid from Aloes.** By P. WESELSKY (Deut. Chem. Ges. Ber., v, 168).

ALOES treated by Hlasiwetz's process (fusion with caustic potash) yields, in addition to orcin and paroxybenzoic acid, a small quantity of a new acid, *alorcinic acid* =  $C_9H_{10}O_3$ . This acid, which is obtained from the mother-liquors of the paroxybenzoic acid, is crystalline, and dissolves with difficulty in cold water, but readily in boiling water, in alcohol, and in ether; by dry distillation it forms a crystalline anhydride; ferric chloride gives no coloration with its aqueous solution, but the liquid when alkalified, gradually becomes cherry-red; hypochlorites give a beautiful purple-red, destroyed by excess of reagent: neutral lead acetate gives no precipitate, but the basic acetate gives a white precipitate becoming red by exposure to air. Fused with caustic potash it forms acetate, and orcin—



whence the author concludes that it is isomeric with acetyl-orcin, and has the formula—



C. R. A. W.



**On Benzyl-sulphonic Acid.** By G. BARBAGLIA (Deut. Chem. Ges. Ber., v, 270).

BENZYL-SULPHONIC acid was prepared by the method of Böhler, whose observations on the course of the reaction and on the properties of the potash salt were confirmed. This salt distilled with potassium cyanide furnished a volatile cyanide which yielded  $\alpha$ -toluic acid on heating with potash; this acid melted at  $75.5^\circ$ , hence the sulphonic acid is a benzyl derivative, *i.e.*,  $C_6H_5.CH_2.SO_3H$ , and not  $C_6H_4 \begin{Bmatrix} CH_3 \\ SO_3H \end{Bmatrix}$ .

On heating benzyl sulphonate of potassium with phosphorus pentachloride, sulphurous acid, thionyl chloride, phosphorus oxychloride, and benzyl chloride were produced: hence the formula of the sulphonate must be either—

$C_6H_5-CH_2-O-S-O-O-K$ , or  $C_6H_5-CH_2-O-O-S-OK$ , for it had been  $C_6H_5-CH_2-S-O-O-OK$ , benzyl sulphochloride should have been formed; and if  $C_6H_5-CH_2-O-O-O-SK$ , phosphorus sulphochloride should have resulted: hence sulphites, *e.g.*, the potassium salt, are  $K-O-S-O-OK$ , and not  $K-S-O-O-OK$ .\*

It may hence be concluded, perhaps, that benzyl-sulphonic acid is not a true sulphonic acid, but a kind of sulphurous ether; true sulphonates having the sulphur in connection with the carbon radical, as is proved by their partial reduction to sulphydrates; and hence a careful revision of the so-called sulphonic acids obtained by oxidising sulphides, sulphocyanates, disulphides, &c., is desirable; also of those obtained by Strecker's reaction (treatment of chlorine, bromine, iodine compounds with neutral sulphites). C. R. A. W.

\* *Note by Abstractor.*—It would seem probable that in the sulphates, sulphur is hexadic, thus orthosulphuric acid  $S(OH)_6$  = so-called hydrate  $SO_4H_2 + 2H_2O$ : of first anhydride,  $S \begin{Bmatrix} (OH)_2 \\ O \\ (OH)_2 \end{Bmatrix}$  = so-called hydrate  $SO_4H_2 + H_2O$ : second anhydride,

$S \begin{Bmatrix} OH \\ O \\ OH \end{Bmatrix}$  (oil of vitriol): third anhydride,  $S \begin{Bmatrix} O \\ O \\ O \end{Bmatrix}$  = sulphur trioxide. Orthosulphates

are known, *e.g.*, Turpeth mineral,  $S \begin{Bmatrix} O \\ O \\ O \\ O \\ O \end{Bmatrix} Hg$ ; and other so-called basic salts may

be represented as salts of the first anhydride.

In the sulphites, sulphur is tetradic, as it is in triethyl-sulphyl iodide  $S(C_2H_5)_3 I$ ; orthosulphurous acid,  $S(OH)_4$  (salts = basic sulphites): first anhydride,  $S \begin{Bmatrix} OH \\ O \\ OH \end{Bmatrix}$  (ordinary sulphites): second anhydride,  $S \begin{Bmatrix} O \\ O \end{Bmatrix}$  = sulphur dioxide.

In sulphonic acids the sulphur may be viewed as hexadic,  $S \begin{Bmatrix} X \\ O \\ O \\ O \\ OH \end{Bmatrix}$ , and in the isomeric sulphurous ethers as tetradic,  $S \begin{Bmatrix} OX' \\ O \\ OH \end{Bmatrix}$ .

**Formation of Orthotoluic Acid by a New Method.** By W. RAMSAY and R. FITTIG (*Zeitschr. f. Chem.* [2], vii, 584—586).

ACCORDING to v. Meyer, salicylic acid is an ortho-, not a meta-compound. This has, however, been doubted, and the authors have, therefore, endeavoured to examine the question by the light of other reactions. To this end they have prepared from toluene the two isomeric sulpho-acids, one of which belongs to the para series, while the other, called by Anna Wolkow, toluene-meta-sulphonic acid, belongs to the same series as salicylic acid, inasmuch as it yields that acid.

As the three toluic acids exhibit differences sufficiently well marked, the examination of the toluic acid obtained from this sulpho-acid must indicate to which series salicylic acid belongs.

By distilling a mixture of the potassium salts of toluene-para-sulphonic acid and the so-called toluene-meta-sulphonic acid with potassium cyanide, and treating the distillate of mixed nitriles with alcoholic potash, ordinary paratoluic acid, mixed with another toluic acid, was obtained.

The calcium salts could not be separated by recrystallisation from water, but from 25 p.c. alcohol, the isomeric calcium salt crystallised readily, leaving the para-toluate in solution. This isomeric toluate contained  $2\text{H}_2\text{O}$ , and gave an acid which crystallised in long shining needles, melting at  $102^\circ$ , and agreed in every respect with ortho-toluic acid, obtained by oxidation of orthoxylene. To dispel all doubt the nitro-acid was prepared, and found to be identical with that obtained from ortho-toluic acid.

The authors regard the formation of ortho-toluic acid in the manner described as conclusive evidence that salicylic acid, and not oxybenzoic acid, belongs to the phthalic acid, or ortho-series.

W. A. T.

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**On the so-called Chloracetene and on the Polymeric Modifications of the Aldehydes.** By A. KÉKULÉ and T. ZINCKE (*Ann. Chem. Pharm.*, cxlii, 125—150; Prelim. Notice, *Deut. Chem. Ges. Ber.*, 1870, 129 and 468).

THE question as to whether all the affinities of the carbon atoms in all organic compounds are saturated or not, induced the authors to undertake an investigation of chloracetene, the generally received formula of which,  $\text{H}_3\text{C}-\text{C}^{\text{II}}\text{Cl}$ , has been made the basis of extensive theoretical speculation (Paterno. *Giorn. di Scienze nat. ed econ.* vi, Palermo, 1870).

Harnitz-Harnitzky (*Ann. Chem. Pharm.*, cxi, 192), first obtained chloracetene by the action of chlorocarbonic oxide on aldehyde vapour, and it has since been prepared and examined by Friedel (*Compt. rend.*, lx, 930; *Ann. Chim. Phys.* [4], xvi, 403), Kraut (*Ann. Chem. Pharm.*, cxlvii, 107), and Stacewicz (*Zeits. Chem.*, 1869, 321). As the authors at first thought that the chloracetene, if not isomeric, might be polymeric with chlorethylene,  $\text{H}_2\text{C}=\text{CHCl}$ , they prepared a quantity of the latter body, and found its boiling-point to be  $-18^\circ$  to  $-17^\circ$ , as given by Regnault.

Chloracetene was then prepared by acting on pure aldehyde with

pure chlorocarbonic oxide under varying conditions, but always with the same result, a liquid being formed which boiled at  $45^{\circ}$  and solidified at  $0^{\circ}$ , as stated by Harnitz-Harnitzky. It was found to behave towards water in the manner observed by him, and to decompose spontaneously when kept, as Friedel states, but the amount of chlorine in it was found to vary in different specimens, never amounting, however, to as much as 57 per cent.

On submitting the liquid to rectification, very peculiar phenomena were noticed, the liquid in the receiver becoming hot, and occasionally entering into ebullition. This circumstance occurred at each rectification, and gave rise to the conjecture that the chlorocarbonic oxide only acted in a manner similar to a ferment. It was ultimately proved by a numerous and carefully conducted series of experiments, not only that the chlorocarbonic oxide converts a portion of the aldehyde into paraldehyde, but that it is also capable, by prolonged contact with paraldehyde, of partially reconverting it into aldehyde, so that the product obtained by the action of chlorocarbonic oxide, either on aldehyde or on paraldehyde, is not a definite compound but simply a mixture of these two modifications in variable proportions, together with more or less chlorocarbonic oxide. A trace of hydrochloric acid acts in a precisely similar manner, and even more energetically than the chlorocarbonic oxide. Sulphuric acid also effects this change, but as it is not volatile, the same phenomena are not observed on distillation, only ordinary aldehyde passing over, whilst the paraldehyde, which boils at a higher temperature, and remains in the retort with the sulphuric acid, is changed by it into ordinary aldehyde during the process of distillation.

Chlorocarbonic oxide can also cause the condensation of aldehyde to crotonaldehyde, with elimination of water, which accounts for the spontaneous decomposition of "chloracetene" observed by Friedel. The authors conclude this section of their paper by explaining the reactions obtained by Friedel and Stacewicz with "chloracetene."

*Polymeric Modifications of the Aldehydes.*—The investigation just noticed having given the authors many opportunities of examining the polymeric modifications of the aldehydes, they thought it advisable to supplement them by special experiments. After noticing the various descriptions given by different chemists of the polymerides of aldehyde, they say that the results of their researches on this point convince them that, besides ordinary aldehyde, there are only two modifications, namely, paraldehyde and metaldehyde. Carefully purified aldehyde does not undergo any change, either when kept or when heated or cooled, polymerisation being invariably caused by the presence of some other substance.

*Paraldehyde.*—In presence of a very small quantity of hydrochloric acid, chlorocarbonic oxide, or sulphurous anhydride, aldehyde gradually becomes hot, the temperature frequently rising to  $38^{\circ}$  or  $40^{\circ}$ . Both zinc chloride and sulphuric acid act in the same way, the addition of a drop of the concentrated acid causing explosive ebullition of the aldehyde; the action of the dilute acid is less energetic. In all these reactions an almost complete transformation into paraldehyde occurs, as is indicated by the change in specific gravity ( $0.986$  at  $15^{\circ}$ ), but the



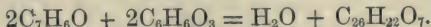
pure substance cannot be directly separated from the product by rectification, as much aldehyde is then regenerated. The best method of separation is to cool the liquid to  $0^{\circ}$ , when the paraldehyde crystallises out, and may be collected and purified by distillation. Paraldehyde is a colourless liquid of peculiar odour, resembling that of acetal. It boils at  $124^{\circ}$ , and crystallises when cooled below  $10^{\circ}$ , forming large transparent prisms, which melt at  $10.5$ . Its specific gravity at  $15^{\circ}$  is  $0.998$ , and its vapour-density three times that of ordinary aldehyde. It is less soluble in hot than in cold water, 100 of the latter dissolving 12 parts at  $13^{\circ}$ . Distillation with sulphuric acid, hydrochloric acid, zinc chloride, or chlorocarbonic oxide, reconverts it into aldehyde. By the action of phosphorus pentachloride it yields ethylidene chloride, as Geuther has observed (*Zeits. Chem.*, 1865, 32), and hydrochloric acid gives the same ethylidene oxychloride that Lieben obtained from ordinary aldehyde (*Ann. Chem. Pharm.*, cvi, 336).

*Metaldehyde.*—This modification has hitherto only been obtained accidentally, the conditions of its formation being unknown; but the authors have found that aldehyde is converted into metaldehyde at a low temperature by the same reagents that cause the formation of paraldehyde at a comparatively high temperature. To prepare it in quantity, a few bubbles of hydrochloric acid, or sulphurous acid, are passed into aldehyde cooled in a freezing mixture, the metaldehyde which crystallises out on standing is removed, and the mother-liquors submitted to distillation, the distillate being collected in a well-cooled receiver; more metaldehyde is then deposited, which is again removed, and the distillation, &c., repeated as above. Calcium chloride also effects the transformation, and that at the ordinary temperature. Metaldehyde crystallises in fine white needles, and that produced by calcium chloride in short, thick, transparent prisms. The crystals, of which measurements by Rath are given, belong to the quadratic system. It is insoluble in water, and but slightly soluble in alcohol, ether, chloroform, or benzol. When heated it sublimes, but ordinary aldehyde is always formed at the same time. Heated to  $112^{\circ}$  to  $115^{\circ}$  in a closed tube, it is completely reconverted into aldehyde, and the same change is produced by distillation with dilute sulphuric acid. The authors consider paraldehyde to have the molecular formula  $C_6H_{12}O_3$ , the aldehyde molecules forming a closed chain by union of their oxygen.

C. E. G.

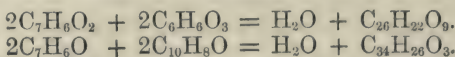
**Compounds of Aldehydes with Phenols.** By A. BÄYER (*Deut. Chem. Ges. Ber.*, v, 280).

BITTER almond oil, heated with pyrogallie acid, yields a resinous red-brown mass, principally consisting of a colourless crystalline compound, formed thus—



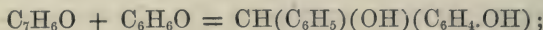
This compound is obtained in a purer condition by mixing together a solution of pyrogallie acid in hydrochloric acid, with a well-agitated emulsion of bitter almond oil, and a large quantity of hydrochloric acid; the crystalline compound then separates, a portion being converted into a red body; the same product results when concentrated

hydrochloric acid is cautiously added to a boiling solution of pyrogallie acid and bitter almond oil in absolute alcohol. This latter process yields similar compounds with salicylic aldehyde and pyrogallie acid, and with bitter almond oil and naphthol—

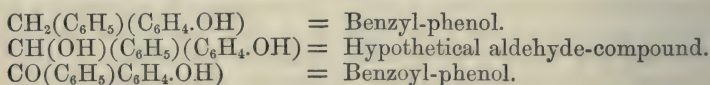


The first compound is almost insoluble in alcohol, these last two soluble.

Most probably the first action in each case is *combination* of the aldehyde and phenol employed, thus (taking phenol and bitter almond oil as examples)—



and subsequently two molecules of this compound coalesce, with elimination of  $\text{H}_2\text{O}$ , thus forming an anhydride, or ether. This hypothetical compound stands in a very simple relation to benzyl-phenol (Paterno *Gaz. Chem. It.*, ii, p. 1, 1872).

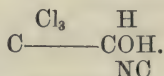


The last named compound is probably obtainable by oxidation of the second, and possibly also by the action of phenol on benzoic acid.

C. R. A. W.

### Some Derivatives of Chloral. By E. HAGEMANN (*Deut. Chem. Ges. Ber.*, iv, 151–154).

1. THE compound of cyanogen with chloral hydrate, lately discovered by Bischoff and Pinner, has been investigated by the author, who gives to it the formula



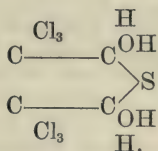
This substance heated with caustic potash, or with sodium carbonate, phosphate, or borate, gives hydrocyanic and formic acids, and chloroform.

From watery solutions it is precipitated in oily drops by strong sulphuric acid, or fuming hydrochloric acid. Melting-point  $58^\circ$ – $59^\circ$  C., solidifying at  $57.5^\circ$ – $58^\circ$ . Begins to boil at  $120^\circ$ , with partial decomposition; the greater part passes over at  $140^\circ$ – $145^\circ$ .

2. Chloral hydrate, hydrocyanic, and fuming hydrochloric acids, heated for 4–5 hours in sealed tubes at  $120^\circ$ – $130^\circ$ , gave, after taking out the ammonium chloride formed by alcohol, a zinc salt of trichlor lactic acid.

3. Sulphuretted hydrogen, by its action on anhydrous chloral, gives a compound insoluble in water, soluble in ether and alcohol, the alco-

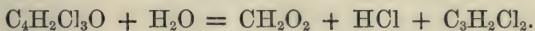
holic solution with lead acetate yielding lead sulphide and chloralhydrate. To this compound the author assigns the formula—



M. M. P. M.

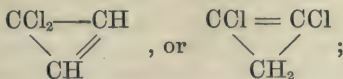
**Constitution of Crotonic Chloral.** By A. PINNER (Deut. Chem. Ges. Ber., v, 205).

ORDINARY chloral treated with alkalis, yields formic acid and chloroform; similarly crotonic chloral gives formic acid, but instead of the product  $\text{C}_3\text{H}_3\text{Cl}_3$ , corresponding to chloroform, dichlorallylene and hydrogen chloride are generated—

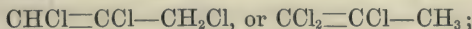


On bromination of this dichlorallylene,  $\text{Br}_2$  is taken up, and then Br substituted for H, so that propane derivatives are not thus obtained, but only propylene derivatives. *Dichlorodibromopropylene*,  $\text{C}_3\text{H}_2\text{Cl}_2\text{Br}_2$ , thus produced by addition of  $\text{Br}_2$ , forms, by the action of alcoholic potash,  $\text{HBr} + \text{C}_3\text{HCl}_2\text{Br} =$  *dichloromonobromallylene*, boiling at  $143^\circ$ ; this body again takes up  $\text{Br}_2$ , and no more, a crystalline body, whose vapour strongly provokes to tears being formed, viz., *dichlorotribromopropylene*  $= \text{C}_3\text{HCl}_2\text{Br}_3$ . Alcoholic potash does not remove HBr from this body, but abstracts the  $\text{Br}_2$  just added, dichloromonobromallylene, boiling at  $143^\circ$ , being reproduced; by digestion with bromine in a sealed tube at about  $160^\circ$ , for several hours, substitution of the last H takes place, *dichlorotetrabromopropylene* being the product.

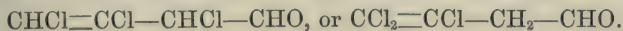
Impure crotonic chloral forms, besides dichlorallylene, *trichloropropylene*,  $\text{C}_3\text{H}_3\text{Cl}_3$ ; this product takes up  $\text{Br}_2$ , giving a propane derivative; and with caustic potash it forms dichlorallylene; pure crotonic chloral forms only dichlorallylene. From the preceding facts the author concludes that dichlorallylene is a compound having an annular formula—



the trichloropropylene that yields dichlorallylene by potash being—



and crotonic chloral being—



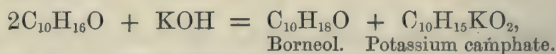
C. R. A. W.



**Compounds belonging to the Camphor Group.** By J. KACHLER  
(Deut. Chem. Ges. Ber., v, 165).

CAMPHOLIC acid obtained by Malin's process (action of potassium on a boiling solution of camphor in petroleum, best of boiling point about  $130^{\circ}$ ), constitutes about 20—22 per cent. of the camphor employed, and has the formula  $C_{10}H_{18}O_2$ , being monobasic. Most of its salts are crystalline, and most easily obtained by double decomposition; it does not form an ethyl salt by treatment with alcohol and hydrogen chloride; nitric acid produces first camphoric acid, then camphoronic acid; bromine and water produces first camphoric acid, then bromocamphoric anhydride, and, lastly, oxycamphoric anhydride; phosphoric chloride forms  $C_{10}H_{17}O.Cl$ , an oil decomposed by water. The calcium salt furnishes on distillation, campholene,  $C_9H_{16}$ ; the substance analysed by Delalande, obtained by this process, and agreeing with the formula,  $C_{19}H_{34}O$ , was probably campholene mixed with some oxidized substance. The acid itself becomes buttery, at about  $80^{\circ}$ , and melts in capillary tubes at  $95^{\circ}$  (Delalande gives  $80^{\circ}$  as the melting point).

Camphic acid obtained by Berthelot's process (fusion of camphor with caustic potash):



is a syrupy liquid, which contains a feebly acid resin; this latter is probably a condensation-product, as it gives off camphor vapours on fusion with caustic potash.

C. R. A. W.

**Relations between the Amides and Anilides of Succinic Acid.** By N. MENSCHUTKIN (Ann. Chem. Pharm., clxii, 165—187).

It has been stated that succinimide  $C_2H_4(CO)_2NH$  possesses the character of a weak acid, the hydrogen of the group  $NH$  being more easily replaced by metals than in other amides, because this group is combined with two  $CO$ . But this hydrogen is only replaced by silver and mercury, which metals also form compounds with other amides.

When succinimide is acted upon by baryta, succinamic acid is formed, which is also easily obtained by boiling the imide with milk of lime. This reaction is, however, not characteristic for succinimide, as it has been supposed to be, since by the same reaction succinanilide is also transformed into succinamic acid, whilst succinanil,  $C_2H_4(CO)_2NC_6H_5$ , as well as phenyl succinamide,  $C_2H_4 \begin{cases} CONH_2 \\ COH_6H_5 \end{cases}$ , yield succinanilic acid. This latter acid was obtained by Gerhardt and Laurent, by acting with ammonia upon succinanil, but only in an impure state. The pure acid prepared by boiling succinanil with baryta or milk of lime, and decomposing the salts with hydrochloric acid, crystallises from boiling water in small needles melting at  $148.5^{\circ}$ .

When succinimide is heated with alcoholic ammonia, it is converted into succinamide. By subjecting succinanil to the same reaction,

phenyl-succinamide is obtained, which crystallises from a hot aqueous solution in flat needles, melting at  $181^{\circ}$ .

From the results of this investigation it appears that an imide may be defined as a compound, which, by combining with water, yields an amic acid, and by combining with ammonia, an amide.

C. S.

**Succinanilide.** By N. MENSCHUTKIN (Ann. Chem. Pharm., clxii, 187).

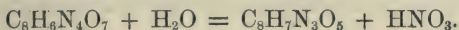
SUCCINANILIDE,  $C_4H_4O_2(NH.C_6H_5)_2$ , is formed, together with succinil, by heating a solution of succinic acid in aniline, and has already been obtained, but in an impure state, by Gerhardt and Laurent. It can be easily separated from succinil, as it is insoluble in water. To purify the compound, it has to be boiled with an alcoholic solution of potash, which does not act upon it. It crystallises from alcohol in flat, shining needles, melting at  $226.5^{\circ}$ — $227^{\circ}$ , and is a very stable body, which is not attacked by nitrous acid, and dissolves in sulphuric acid and nitric acid, without alteration. On heating it with hydrochloric acid for some hours in sealed tubes to  $100^{\circ}$ , it is completely decomposed into aniline and succinic acid.

C. S.

**Derivatives of Uramidobenzoic Acid.** By P. GRIESS (Deut. Chem. Ges. Ber., v, 192—203, and Proc. Roy. Soc., xx, 168—178).

In a previous note (Deut. Chem. Ges. Ber., ii, 434) it was stated that by the action of strong nitric acid upon uramidobenzoic acid, *dinitro-uramidobenzoic acid*,  $C_8H_6(NO_2)_2N_2O_3$ , is formed. This compound, although apparently a homogeneous body, consists, as the following facts show, of a mixture of three isomerides, which, owing to the great similarity of their properties, cannot be separated from each other.

When the solution of the three dinitro-acids in aqueous ammonia is boiled for some time, they are converted into the mono-nitro-acids—



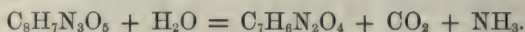
By adding barium chloride to the hot solution on cooling, the barium salt of the  $\beta$ -acid separates in needle-shaped crystals. On concentrating the mother-liquor of this salt by evaporation, the salt of the  $\alpha$ -acid separates in microscopic needles; the barium salt of the third acid is obtained by boiling the mother-liquor from the previous salt to dryness, and washing the residue with water. It crystallises from hot water in bright yellow scales.

The three acids set free from the barium salts by means of hydrochloric acid, have the following properties:—

$\alpha$ -Nitrouramidobenzoic acid,  $C_8H_7(NO_2)N_2O_3$ , crystallises in bright yellow needles or small plates; it is very slightly soluble in cold water, sparingly in hot, and freely in hot alcohol.

$\beta$ -Nitrouramidobenzoic acid crystallises in slender yellow needles, and also much more freely soluble in alcohol than in water.

$\gamma$ -Nitrouramidobenzoic acid is very slightly soluble in all neutral solvents, and forms small yellow scales. When the free acid and its salts are boiled with water for a considerable time, the following decomposition takes place:—



The  $\alpha$ - and  $\beta$ -acids are reduced by tin and hydrochloric acid to the amido-acids.  $\alpha$  amido-uramidobenzoic acid,  $\text{C}_8\text{H}_7(\text{NH}_2)\text{N}_2\text{O}_3$ , is but slightly soluble in hot water, and less so in alcohol; it forms a white, silver-salt,  $\text{C}_8\text{H}_5\text{N}_3\text{O}_3\text{Ag}$ , and a hydrochloride,  $\text{C}_8\text{H}_5\text{N}_3\text{O}_3\cdot\text{HCl}$ , which is almost insoluble, even in very dilute hydrochloric acid.  $\beta$  amido-uramidobenzoic acid is very little soluble in water, and, curiously enough, does not combine with acids, but forms metallic salts, having the formula,  $\text{C}_8\text{H}_5\text{N}_3\text{O}_3\text{M}'$ . On boiling this acid with hydrochloric acid or baryta water, it gives off ammonia, and a new acid is formed, which may be regarded as amidobenzoic acid in which one atom of hydrogen is replaced by  $(\text{CO})\text{N}$ , and may therefore be called  $\beta$ -amidocarboxamidobenzoic acid,  $\text{C}_7\text{H}_4(\text{NH}_2)(\text{CO}(\text{N}))\text{O}_2$ ; this acid forms white nodules, insoluble in all neutral solvents.

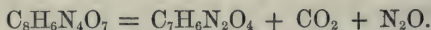
$\gamma$ -Nitrouramidobenzoic acid is not reduced by the action of tin and hydrochloric acid, but undergoes the following decomposition:—



The new compound is  $\gamma$ -amidocarboxamidobenzoic acid. It forms white needles, which are almost insoluble in water, alcohol, and ether.

By the action of nitric acid, the mononitro-acids are again converted into the dinitro-acids, which can thus be obtained in a pure state. They closely resemble one another, forming yellowish white needles, which are readily soluble in alcohol and ether, but scarcely soluble in cold water. The barium-salts of the  $\alpha$ - and  $\beta$ -acids are very sparingly soluble; that of the former crystallises in microscopic needles, that of the latter is amorphous. Barium  $\gamma$ -dinitrouramidobenzoate is somewhat more readily soluble, and forms long slender yellow needles.

All three of the dinitro-acids are converted into the corresponding nitroamidobenzoic acids, when their aqueous solutions are boiled for a considerable time—



$\alpha$ -Nitroamidobenzoic acid,  $\text{C}_7\text{H}_4(\text{NO}_2)(\text{NH}_2)\text{O}_2$ , is readily soluble in hot alcohol, but only sparingly in water, and forms yellow prisms. The barium salt  $(\text{C}_7\text{H}_5\text{N}_2\text{O}_4)_2\text{Ba} + 3\text{H}_2\text{O}$  crystallises in yellowish-red needles, and is readily soluble in water.

$\beta$ -Nitroamidobenzoic acid crystallises from hot alcohol in clusters of glistening, yellowish-red needles, or small plates. When gently heated it sublimes in shining rhombic plates, without previous melting. Its barium salt  $(\text{C}_7\text{H}_5\text{N}_2\text{O}_4)_2\text{Ba} + 2\text{H}_2\text{O}$  is only slightly soluble in boiling water, and crystallises in bright, yellowish-red prisms.

$\gamma$ -Nitroamidobenzoic acid is very readily soluble in hot water and cold alcohol and ether. It forms yellow prisms, which melt when heated to a brown oil, and decompose with slight explosion at a higher



temperature. The barium salt  $(C_7H_5N_2O_4)_2Ba + 7H_2O$  is easily soluble, even in cold water.

On gently warming these three nitroamido-acids with tin and hydrochloric acid, the corresponding diamido acids are formed. *α*-diamidobenzoic acid,  $C_7H_4(NH_2)_2O_2$  is sparingly soluble in hot water, and crystallises in minute but well-defined short prisms. It is remarkable for the extremely sparing solubility of the sulphate,  $C_7H_5N_2O_2 \cdot SO_4H_2$ .

The *β*-diamido acid is rather readily soluble in hot water, and forms pale yellow plates. Its sulphate has the composition  $[C_7H_4(NH_2)_2O_2]_2SO_4H_2$ , and is a little more soluble than that of the *α*-acid. The *γ*-acid crystallises in long, yellowish-white needles; the sulphate  $(C_7H_5N_2O_2)_2SO_4H_2 + 1\frac{1}{2}H_2O$  forms white, six-sided tables, and is almost as insoluble as that of the *α*-acid.

When the *α*-diamido-acid is dissolved in warm dilute hydrochloric acid, insufficient to dissolve the whole, and the filtered solution is mixed with sodium nitrite, an explosive compound, crystallising in long needles, is formed. This body has no acid properties, but combines readily with acids, forming well crystallised salts. Its formula is probably  $C_{14}H_{13}N_5O_4$ . In presence of free hydrochloric acid, this basic compound is not formed, but nitrogen is evolved, and an amorphous reddish-brown acid is deposited.

The hydrochlorides of the two other amido-acids behave differently with sodium nitrite; they both yield azo-acids. That from the *β*-compound is very sparingly soluble in water, and forms white, short needles, which, when heated in the dry state, melt and blacken, a small portion subliming, but the greater part being completely decomposed. The barium salt  $(C_7H_4N_3O_2)_2Ba + 4H_2O$  is readily soluble in hot water, and crystallises in slender, colourless needles. The *γ*-azo-acid crystallises in long, hair-like, silky needles. It is more soluble than the *β*-acid; when gently heated it melts to a yellow oil, with partial sublimation taking place; at a higher temperature it decomposes, with a slight explosion. The white needles of its barium salt  $(C_7H_4N_3O_2)_2Ba + 2H_2O$ , are only sparingly soluble in hot water.

When either of the diamido-acids is submitted to dry distillation, it splits up into carbon dioxide and phenylene-diamines. That from the *α*-acid is identical with the diphenylamine which is obtained from the nitroaniline prepared from substituted anilides. The *β* and *γ* acids yield *one* and the *same* phenylene-diamine, which, however, is not identical with that derived from dinitrobenzene, but is a new isomeric modification. It crystallises from hot water in white, rectangular, four-sided tables, melting at  $99^\circ$ , and boiling at about  $252^\circ$ . The sulphate,  $C_6H_4(NH_2)_2SO_4H_2 + 1\frac{1}{2}H_2O$ , crystallises in pearly scales. The platinum salt is precipitated in form of brownish red needles. When ferric chloride is added to a solution of the base in hydrochloric acid, ruby-red needles form, consisting of the hydrochloride of a new base, which probably has the composition,  $C_{12}H_{10}N_4$ .

There is a fourth diamidobenzoic acid known, which Voit has obtained by reducing dinitrobenzoic acid. This body is distinguished from its isomerides, not only by its physical properties, but especially by not yielding a volatile base when submitted to distillation, being completely carbonised with evolution of ammonia.

**Isuretine, a Base isomeric with Urea.** By W. LOSSEN and P. SCHIFFERDECKER (*Zeitschr. f. Chem.* [2], vii, 594—597).

AN alcoholic solution of hydroxylamine digested with strong hydrocyanic acid at  $40^{\circ}$ — $50^{\circ}$ , and then evaporated, furnishes large crystals of the new base, which may be rendered pure by redeposition from warm spirit of wine.

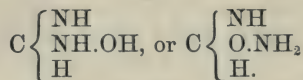
Isuretine,  $\text{N}_2\text{CH}_4\text{O}$ , is very easily soluble in water, less readily in alcohol, slightly in ether, not in benzene. It has a strong alkaline reaction, melts with incipient decomposition at  $104^{\circ}$ — $105^{\circ}$ . The crystals sometimes resemble those of urea. Its solutions give with copper sulphate a dirty green, with lead nitrate a white precipitate, with mercuric chloride a precipitate which is at first bulky and yellowish-white, afterwards denser and dark yellow. With silver solutions no precipitate is deposited, but on applying heat the silver is reduced. Ferric chloride gives a reddish-brown colour, which disappears on addition of hydrochloric acid.

The hydrochloride,  $\text{N}_2\text{CH}_4\text{O}.\text{HCl}$ , crystallises in deliquescent rhombic tables, excessively soluble in water, fusible at about  $60^{\circ}$ . The sulphate,  $(\text{N}_2\text{CH}_4\text{O})_2\text{H}_2\text{SO}_4$ , acid oxalate,  $\text{N}_2\text{CH}_4\text{O}.\text{C}_2\text{O}_4\text{H}_2$ , and picrate,  $\text{N}_2\text{CH}_4\text{O}.\text{C}_6\text{H}_3(\text{NO}_2)_3\text{O}$ , are all crystallisable.

*Decomposition of Isuretine by Heat.*—Heated beyond its melting point, isuretine readily decomposes, evolving a small quantity of permanent gas, and giving a considerable sublimate of ammonium carbonate. A yellowish amorphous residue is left, from which boiling water extracts a yellowish substance very slightly soluble in water, and presenting the composition and essential characters of ammelide,  $\text{N}_9\text{C}_6\text{H}_9\text{O}_3$ . The portion of the residue insoluble in boiling water has substantially the composition of ammelide, the number obtained for the nitrogen being, however, a little too high. This residue boiled with nitric acid furnishes cyanuric acid.

*Decomposition of Isuretine by Hot Water.*—An aqueous solution of isuretine evaporated on a water-bath undergoes decomposition, with evolution of nitrogen, ammonia, and carbonic anhydride. For want of material, the residue has not yet been completely examined; however, two compounds, urea and biuret, have been separated from it and identified.

Its decomposibility at high temperatures, and the facility with which isuretine colours ferric chloride and reduces silver salts, may be explained on the hypothesis that it is a derivative of hydroxylamine. One of the two following structural formulæ would then probably represent it:—



W. A. T.

**Contributions to the History of the Ethylene Bases.** By A. W. HOFMANN (*Deut. Chem. Ges. Ber.*, v, 240—248).

THE author having prepared a considerable quantity of ethylenediamine from the residues of the chloral manufacture (this Journal,

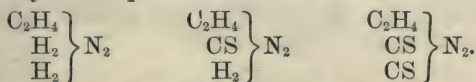
xxiv, 930), has repeated with this base some of the reactions which have given results with the monamines.

1. *Action of Carbon Disulphide on Ethylene-diamine.*—An alcoholic solution of ethylene-diamine mixed with carbon disulphide deposits, in a short time, a white and nearly amorphous compound, having the composition  $C_3H_8N_2S_2 = (C_2H_4)H_4N_2, CS_2$ . It is almost insoluble in alcohol and ether, but dissolves in warm water with partial decomposition, and, provided the solution has not been boiled, is again deposited on cooling in prismatic crystals. This compound does not yield ethylene-diamine when treated with alkalis, and is therefore not the ethylene-sulphocarbonate of ethylene-diamine.

*Ethylene-sulphocarbamide, Ethylene-sulphourea.*—On boiling the above-mentioned compound with water, dilute acids, or solutions of metallic salts, sulphuretted hydrogen is given off, and ethylene sulpho-

urea,  $C_3H_6N_2S = C_2H_4 \left\{ \begin{smallmatrix} CS \\ H_2 \end{smallmatrix} \right\} N_2$ , is formed:  $C_3H_8N_2S_2 = C_3H_6N_2S + H_2S$ .

It is soluble in water, and crystallises from its aqueous solution in prismatic crystals possessing an extremely bitter taste. It is only slightly soluble in ether, but readily in alcohol. It melts at  $194^\circ$ , and is decomposed at a higher temperature. A mercury-compound,  $2C_3H_6N_2S \cdot 3HgCl_2$ , and a bright yellow amorphous platinum-compound,  $2C_3H_6N_2S \cdot PtCl_4$ , have been prepared. On heating the urea with strong sulphuric acid, diluting with water, and adding platinum-chloride, a second salt is obtained, crystallising in long needles,  $2(C_3H_6N_2S \cdot HCl) \cdot PtCl_4$ . When this salt, however, is decomposed by sulphuretted hydrogen and platinum chloride added to the hydrochloric acid solution, the original *amorphous* platinum compound is precipitated. This urea, which is intermediate between ethylene-diamine and ethylene-sulphocarbamide—



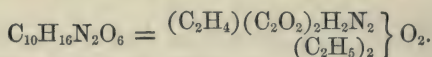
is very stable, not being altered by long digestion at a high temperature with carbon disulphide or with carbon disulphide and lead oxide. The author had hoped by this means to convert it into the mustard oil.

*Ethylene-diamine Sulphocyanate.*—Ethylene-diamine hydrochloride and silver sulphocyanate have no action on one another, but the salt can be readily prepared by saturating ethylene-diamine with sulphocyanic acid. The new compound crystallises in large transparent prisms, which soon become opaque. It is insoluble in ether, very soluble in alcohol, and still more so in water. Even below its melting point, which is about  $145^\circ$ , it splits up into ammonium sulphocyanate and ethylene-sulphourea, no mustard oil being formed. This is quite analogous to the decomposition which aniline sulphocyanate undergoes when heated (Hofmann, *Ann. Ch. Pharm.*, lxx, 143).

2. *Ethylene-diamides.*—A mixture of benzoyl chloride and ethylene-diamine, after it has become cool, solidifies to a crystalline mixture of ethylene-diamine hydrochloride and *ethylene-dibenzoyl-diamide*,



$$\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2 = \left( \begin{array}{c} \text{C}_2\text{H}_4 \\ (\text{C}_7\text{H}_5\text{O})_2 \\ \text{H}_2 \end{array} \right) \text{N}_2.$$
 The latter crystallises in needles, which are slightly soluble in alcohol, but insoluble in water. By the action of chloral on ethylene-diamine, ethylene-diformyl-diamide,  $(\text{C}_2\text{H}_4)(\text{CHO})_2\text{H}_2\text{N}_2$  is formed, with elimination of chloroform. It is a transparent syrup, which is easily decomposed into ethylene-diamine and formic acid by the action of alkalis or acids. In a similar way pure ethylformamide, boiling at  $199^\circ$ , may be obtained from ethylamine and chloral. A mixture of ethyl oxalate and a strong alcoholic solution of ethylene-diamine becomes almost solid, from deposition of ethylene oxamide,  $\text{C}_4\text{H}_6\text{N}_2\text{O}_2 = \left( \begin{array}{c} \text{C}_2\text{H}_4 \\ \text{C}_2\text{O}_2 \\ \text{H}_2 \end{array} \right) \text{N}_2$ . It is an amorphous substance, scarcely soluble either in alcohol or water. The mother-liquors from this, on evaporation, leave ethyl ethylene oxamate—



This compound crystallises in white scales, which are very soluble in alcohol and water.

C. E. G.

**The Solidifying Point of Aniline.** By E. LUCIUS (Deut. Chem. Ges. Ber., iv, 154—155.)

THE author noticed that some aniline he had in his laboratory became solid during last winter's cold. He found that it remelted at  $-8^\circ$ , and solidified on again cooling to this point. These results are confirmed by Hofmann, who experimented with absolutely pure aniline. Aniline mixed with toluidine, picoline, &c., exhibits quite a different solidifying point from that of pure aniline.

M. M. P. M.

**New Decomposition-product from Commercial Aniline.** By R. BRAUN and PH. GREIFF (Deut. Chem. Ges. Ber., v, 276).

ON distillation of large quantities of aniline with a little lime, it was noticed that the last portions of the distillate would not wholly dissolve in hydrochloric acid. The insoluble portion was at first taken for anthracene, but has been since identified with the *carbazol* of Graebe and Glaser, its melting point being  $238^\circ$ , and its other properties corresponding. It is extremely improbable that the carbazol was contained in the original aniline. It appears to be produced when the nearly dry mixture of lime and aniline comes in contact with the hot sides of the vessel employed.

C. R. A. W.

**Derivatives of Benzidine.** By I. STRAKOSCH (Deut. Chem. Ges. Ber., v, 236—240).

By the action of nitric acid upon benzidine, only oxidation-products are formed, but no nitro-compounds. To obtain the latter, benzidine must first be converted into acetobenzidine, which is easily effected by boiling benzidine with glacial acetic acid for two hours.

*Acetobenzidine*,  $C_{12}H_8(NH.C_2H_3O)_2$  is insoluble in water, and crystallises from hot alcohol in white needles. It is a very stable compound, not so easily decomposed by stronger acids as acetanilide.

Cold nitric acid converts it into *dinitracetobenzidine*,  $C_{12}H_6(NO_2)_2(NH.C_2H_3O)_2$ , a yellow crystalline powder which, when boiled with caustic potash yields *dinitrobenzidine*,  $C_{12}H_6(NO_2)(NH_2)_2$ , a light red crystalline powder, insoluble in water, but soluble in hot alcohol, from which solution it separates after some time in larger crystals having a beetle-green lustre. The hydrochloride forms shining dark yellow plates, and is a very unstable body, being readily decomposed by water as well as by heat. Experiments made for the purpose of obtaining an amidobenzidine failed. By acting on the dinitro-compound with tin and hydrochloric acid, the nitrogen of the nitro group separates in form of ammonia, and benzidine is formed, whilst by heating it with ammonium sulphide only indefinite brown substances were obtained.

On digesting benzidine with carbon disulphide, the compound  $C_{12}H_8 \left\{ \begin{smallmatrix} NH \\ NH \end{smallmatrix} \right\} CS$  is obtained, a body quite insoluble in all common solvents. Besides this substance, another, having the same composition, but soluble in alcohol, is formed in smaller quantities, to which perhaps the above formula should be given, whilst the insoluble body might be a polymericide.

C. S.

**Diphenine.** By I. LERMONTOFF (Deut. Chem. Ges. Ber., v, 231—236).

DIPHENINE, which Gerhardt and Laurent first obtained by reducing dinitroazobenzene with hot alcoholic ammonium sulphide, is generally regarded as diamido-azobenzene,  $C_{10}H_8N_2(NH_2)_2$ . But as Hofmann has found that azobenzene,  $C_{12}H_{10}N_2$ , readily combines with hydrogen, forming hydrazobenzene,  $C_{12}H_{12}N_2$ , it appeared probable that diphenine was diamido-hydrazobenzene. The author therefore prepared pure diphenine, and analysed it and some of its salts, and found that its composition was really  $C_8H_{10}N_2(NH_2)_2$ .

When dinitroazobenzene is acted upon by cold ammonium sulphide, no diphenine is formed, but *hydro-dinitroazobenzene*,  $C_8H_{10}N_2(NO_2)_2$ , just as azobenzene under these circumstances yields hydrazobenzene.

Hydro-dinitroazobenzene is insoluble in water, and crystallises from boiling alcohol in long yellow needles, melting at  $220^\circ$ . Oxidising agents re-convert it into dinitroazobenzene. When the hydro-compound is heated to  $220^\circ$ — $250^\circ$ , it splits up into dinitroazobenzene and nitraniline, just as hydrazobenzene is decomposed by distillation into azobenzene and aniline. The nitraniline thus obtained melts at  $110^\circ$  and is identical with that prepared from dinitrobenzene. As was to be expected,

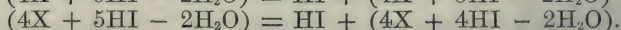
hydro-dinitroazobenzene is readily converted into diphenine by the action of hot ammonium sulphide. Hofmann has already found that by the continued action of ammonium sulphide upon dinitroazobenzene  $\beta$  phenylene-diamine is formed. This body is always produced when dinitroazobenzene or its reduction-products is heated with ammonium sulphide in closed tubes for some hours to  $100^{\circ}$ . The compound called hydro-azaniline, which Haarhaus (*Ann. Chem. Pharm.*, cxxxv, 164) obtained by the action of sodium amalgam upon nitraniline, is isomeric with diphenine, and not identical, as might have been expected, although it also yields  $\beta$  phenylene-diamine when acted upon by ammonium sulphide under pressure.

C. S.

### Contributions to the History of the Opium Alkaloids (Parts IV and V). By C. R. A. WRIGHT (Proc. Roy. Soc., vol. xx\*).

THESE papers contain a description of the products obtained by the action of hydriodic acid on morphine in presence of phosphorus, and of phosphoric acid on codeine. In the first case, whether the action takes place at  $100^{\circ}$ ,  $110^{\circ}$ — $115^{\circ}$ , or at  $130^{\circ}$ , the same substance results, viz.,  $C_{68}H_{82}I_2N_4O_{10}, 4HI$ , or  $(4X + 6HI - 2H_2O)$ , where X represents a hypothetical base,  $C_{17}H_{21}NO_3$ . In this respect morphine differs from codeine, which gives rise at these three temperatures respectively to three different products, viz.,  $(4X + 6HI)$ ,  $(4X + 6HI - 2H_2O)$ , and  $4Y + 6HI - 2H_2O$ , where Y represents another hypothetical base,  $C_{17}H_{21}NO_2$  (page 150 of this volume).

The product from morphine appears to be identical with the second of these products from codeine, no difference being discernible in chemical reactions, physical properties, or physiological action. When long boiled with water, the elements of HI are removed in each case, the resulting products being also apparently identical in each case respectively.



Before the second of these reactions is completed, in the case of the morphine derivative, a product is formed which may be either a mixture of  $4X + 5HI - 2H_2O$  and  $(4X + 4HI - 2H_2O)$  in equivalent quantities, or a single substance of formula  $(8X + 9HI - 4H_2O) = C_{136}H_{161}IN_8O_{20}, 8HI$ . A body of exactly the same constitution has also been obtained by the same process from the codeine derivative; and as it does not seem probable that mixtures in equivalent quantities would be obtained in two distinct cases, it is inferred that the body is really a single substance, and not a mixture, an inference justified by the fact that a codeine derivative (described in the second of these papers) which undoubtedly contains  $C_{136}$  (its formula being  $C_{136}H_{153}IN_8O_{20}, 8HI$ ) has been obtained from a polymeride of codeine. Moreover, the experiments described in the second paper show that the group  $C_{68}$  is contained in substances that are derived from a lower polymeride of codeine than that from which these iodized bodies are derived, and hence they must contain at least  $C_{136}$ .

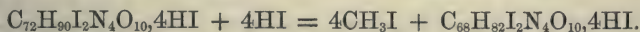
\* Part iv, p. 203; part v, not yet published in the Proceedings.



Reasons are given for the conclusion that morphine is *not* (as was at first supposed) produced from codeine by the action of hydriodic acid. Although the resulting product is the same in each case, the reactions by which it is produced are different. With codeine, the reaction is probably



and—



In other words, polymerisation *precedes* methyl elimination. With morphine—

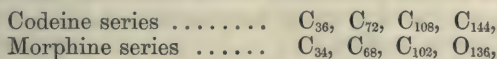


hence the non-formation of Y bases from morphine is partly accounted for, the O of the (O.CH<sub>3</sub>) group in codeine (polymerised) being affected by the removal of CH<sub>3</sub>, and thus being in a *quasi* nascent state.

From the previous work on codeine and morphine (partly in conjunction with the late Dr. Matthiessen) these conclusions are drawn:—

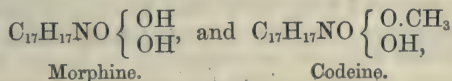
(1.) The actions of HCl, HBr, and HI on these bases are entirely different, the first giving rise (principally) to products derived from ordinary (*i.e.*, not polymerised) codeine; the second to bodies of this class, and also to “tetra” bases; and the last only to “tetra” bases, with simultaneous addition of hydrogen.

(2.) Probably polymerides containing—

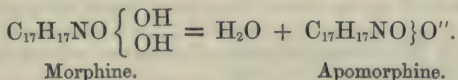


are obtainable from the bases, and serve as the foundation for corresponding series of derivatives. (Researches in progress indicate that ordinary codeine and morphine contain respectively C<sub>36</sub> and C<sub>34</sub>, and not C<sub>18</sub> and C<sub>17</sub> as hitherto supposed. The lower formulæ are adhered to in this paper for clearness of comparison with the former papers.) From this facility of polymerisation the speculation is made that pyridine radicals may be contained in these bases, a speculation apparently borne out by experiments now in progress in conjunction with E. Ludwig Mayer.

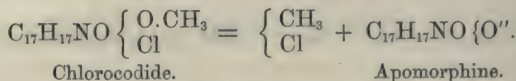
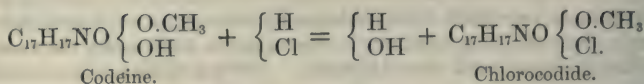
(3.) Codeine appears to be a species of methylic ether of morphine, their relative formulæ being (old formulæ, C<sub>18</sub> and C<sub>17</sub>)—



and hence the same apomorphine is obtainable from both by the reactions—



And—



(It appears not improbable, from researches in progress, that apomorphine has a much higher formula than this, being probably  $\text{C}_{68}\text{H}_{68}\text{N}_4\text{O}_8$ , i.e., a derivative from the  $\text{C}_{68}$  polymeride.)

(4.) From Schiff's distinction between phenols and anisols (*Ann. Chem. Pharm.*, clix, 158), that the first give colours with ferric chloride and the second not, it is not improbable that codeine and morphine contain benzene radicals in their formulæ.

Dr. Reginald Stocker finds that the physiological action of the derivatives ( $4\text{X} + 6\text{HI} - 2\text{H}_2\text{O}$ ) and ( $4\text{X} + 5\text{HI} - 2\text{H}_2\text{O}$ ) is the same whether these products are obtained from morphine or codeine. The action is not nearly so powerful as that of the  $\text{HCl}$  and  $\text{HBr}$  derivatives formerly described, the most marked symptoms observed (after doses of 0.1 to 0.5 gram of each compound had been given to an adult terrier by the mouth) being repeated defæcation in a short time, the stools being looser than ordinarily, and of a dark greenish colour.

The previous results having led to the conviction that codeine and morphine are capable of forming polymerides containing in their formulæ double, treble, quadruple . . . . . the number of symbols contained in the formulæ of the original alkaloids respectively, experiments were made to obtain these polymerides before their further alteration by secondary reactions. The action of acetic acid on codeine was examined, with negative results, not more than traces of a compound (acetyl-codeine?) different from the original codeine being obtained after 64 hours' digestion at  $100^\circ$  of 1 part of alkaloid to 3 of glacial acid. The action of phosphoric acid, however, was found to be precisely that anticipated, when pushed far enough. On boiling 1 part codeine, 3 glacial acid, and 5 of water very gently in an open vessel until the temperature rises to close upon  $200^\circ$ , a considerable quantity of the codeine becomes polymerised, forming simultaneously *dicodine*,  $\text{C}_{72}\text{H}_{84}\text{N}_4\text{O}_{12}$ \* and *tetracodine*,  $\text{C}_{144}\text{H}_{168}\text{N}_8\text{O}_{24}$ , which are sharply distinguished from codeine and from each other by their physical properties and chemical reactions. The first of these bases forms a crystalline hydrochloride, whose water of crystallisation is lost at  $100^\circ$ , the base itself being amorphous and *immediately* precipitated from its salts by sodium carbonate. (Codeine is crystalline, and not immediately precipitated by sodium carbonate, and its hydrochloride loses none (Matthiessen and Wright, *Proc. Roy. Soc.*, xviii, 87) of its water of

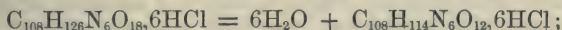
\* As mentioned in Part iv, experiments now in progress indicate that the formula of codeine is  $\text{C}_{36}\text{H}_{42}\text{N}_2\text{O}_6$ , and not  $\text{C}_{18}\text{H}_{21}\text{NO}_3$ .

crystallisation on drying in the water-bath at a temperature probably slightly below  $100^{\circ}$ .) The second is amorphous, and forms amorphous salts, and differs from codeine and dicodeine by being insoluble in ether.

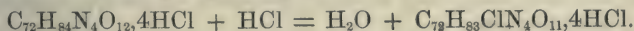
The properties of these new polymerides suggested their respective identity with the "isomeride of codeine" obtained by Matthiessen and Armstrong (this Journal [2], ix, 56), by the short-continued action of diluted sulphuric acid on codeine, and with the "amorphous codeine" of Anderson (Ed. *Phil. Trans.*, vol. xx [1], p. 57) obtained by the same agent after longer action. On repetition of the processes of these chemists, the resulting products were found to be apparently identical with the products of the action of phosphoric acid, with only this difference, that Armstrong's process appears to give rise to a small quantity of another polymeride (in addition to dicodeine), which is non-crystalline and soluble in ether. Its hydrochloride utterly refuses to crystallise, and its reactions are different from those of either of the other polymerides. The dicodeine is separable from this by repeated crystallisation of its hydrochloride until the salt ceases to give a *blood-red* coloration on addition of nitric acid, the tint produced by pure dicodeine being a yellow orange, not intense. From the circumstance that in many instances this polymeride exhibits similarity to dicodeine, but in others to tetracodeine, it is regarded as probably intermediate, *i.e.*, as *tricodeine*,  $C_{108}H_{126}N_6O_{18}$ .

That dicodeine is capable of direct polymerisation to tetracodeine (*i.e.*, that this latter is not produced from codeine directly, but through the first formation of dicodeine and its subsequent alteration), was shown by converting dicodeine into tetracodeine by the action of dilute sulphuric acid. No tricodeine was thereby produced, a result corroborative of the formula attributed to this substance, in so far as it is thereby proved not to be a derivative of dicodeine, but to be produced directly from codeine by a polymerising reaction.

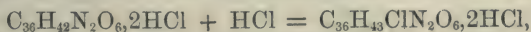
Hydrochloric acid acts on these polymerides very differently. On tetracodeine it has no action whatever after six hours' ebullition; with tricodeine at  $100^{\circ}$  for  $1\frac{1}{4}$  hour it produces the following reaction:—



and with dicodeine the following:—



(With codeine, as will be shown in a future paper, the first action appears to be to produce an addition-product, thus:—



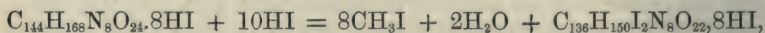
from which water is subsequently eliminated.)

This action therefore proves that dicodeine cannot have a formula less than  $C_{72}H_{84}N_4O_{12}$ , for the resulting product,  $C_{72}H_{83}ClN_4O_{11}$ , is readily soluble in ether, and hence has not been formed by polymerisation of the dicodeine to the tetra series. The reactions of codeine, however, lead to  $C_{36}H_{42}N_2O_6$  as the lowest formula consistent with its reactions, and those of tetracodeine, as shown below, to  $C_{144}H_{168}N_8O_{24}$ , as its lowest



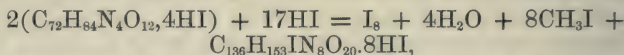
formula; hence the names. The product  $C_{108}H_{114}N_6O_{12}$  from tricodeine much resembles in its properties the "apocodeia" of Matthiessen and Burnside (*Proc. Roy. Soc.*, xix, 71), produced by the action of zinc chloride on codeine; probably, therefore, this action gives rise to a mixture of "apo" derivatives of the general formula  $(C_{18}H_{19}NO_2)_n \cdot nHCl$  wherein the derivative in which  $n = 6$  predominates.

Hydriodic acid in conjunction with phosphorus acts on dicodeine and tetracodeine differently, the actions being instructive on comparison with that formerly shown (Part III) to take place with codeine. Tetracodeine gives rise to the reaction (on boiling until the boiling point has risen to  $130^\circ$ )—

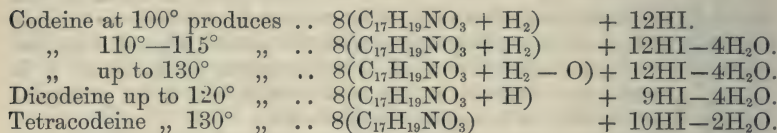


the product being the hydriodide of a tetra base insoluble (or nearly so) in ether.

Dicodine becomes polymerised to a tetra base nearly insoluble in ether, but in addition to methyl-elimination, hydrogen-addition takes place—



the formula of the product proving that the minimum formula of tetracodeine must contain  $C_{144}$ , and not  $C_{72}$  only. The hydrogen addition, however, does not go so far as it does when ordinary codeine is employed; thus—



Hence dicodeine is in this respect strictly intermediate between codeine and tetracodeine, and this result furnishes a further proof of the conclusion arrived at in Part IV, that the addition of hydrogen *precedes* polymerisation, and that therefore morphine is not produced from codeine by the action of hydriodic acid; for if polymerisation even to dicodeine took place, only H would be added on for  $C_{17}$ , and not  $H_2$ , as is actually the case.

The observed fact that the addition of the elements of HI precedes the elimination of  $H_2O$  with codeine (as well as the same circumstance observed with HCl and codeine and HCl and morphine, according to experiments now in progress) tends to show that the action is not, as was at first supposed (Matthiessen and Wright, *Proc. Roy. Soc.*, xviii, 85), a true replacement of hydroxyl by iodine (or chlorine). This point is under examination.

Dr. R. Stocker has examined the physiological action of the hydrochlorides of these polymerides, 0.1 gram of the anhydrous salt being subcutaneously injected into adult cats and dogs. The main results of 16 experiments are given at the end of the annexed table, and tend to show, together with the chemical and physical observations, that what-

ever may be the theoretical explanation of the process here termed *polymerisation* (symbolically denoted by multiplication of the formula), it represents a true chemical reaction, *i.e.*, the production of a resulting body having different properties from those possessed by the original substance.

From the known characters of the quinine and cinchonine isomerides, it seems not improbable that the different modifications are really polymerides; and from certain observed properties and reactions of cotarnine and opianic acid (the decomposition-products of narcotine) the speculation is made that narcotine has probably double the formula hitherto ascribed to it; and from those of Matthiessen's dimethylnornarcotine, methylnornarcotine, and nornarcotine, it appears not improbable that these bases are derivatives not of narcotine itself, but of its polymerides. Similarly the crystalline and amorphous modifications of thebaine described by Hesse (*Ann. Chem. Pharm.*, cliii, 47) are probably dithebaine and tetrathebaine respectively.

The following table exhibits the principal differences between codeine and its polymerides, above described :—

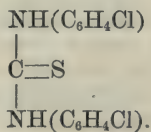
Reagent, &c.	Codeine.	Dicodeine.	Tricodeine.	Tetracodeine.
Alcohol.	Soluble.	Soluble.	Soluble.	Soluble.
Ether.	Soluble.	Soluble.	Soluble.	Insoluble.
Character of base.	Crystalline; stable in the air.	Amorphous; stable in the air.	Amorphous; very slowly oxidizes while moist.	Amorphous; very slowly oxidizes while moist.
Character of hydrochloride.	Crystallises with 2H <sub>2</sub> O for C <sub>18</sub> ; not lost at 100°.	Crystallises with 3H <sub>2</sub> O for C <sub>18</sub> ; lost at 100°, and partially at lower temperatures.	Non-crystalline; extremely deliquescent.	Non-crystalline; deliquescent.
Ferric chloride.	Nil.	Nil, when pure.	No colour at first; reddish-purple on standing.	Reddish-purple colour immediately.
Nitric acid.	Light orange.	Light orange.	Blood-red.	Blood-red.
Potassium dichromate and sulphuric acid.	Nil.	Nil.	Evanescent red.	Evanescent red.
Sodium carbonate and solution of hydrochloride.	No immediate precipitate; crystals on standing.	Instantaneous amorphous precipitate, but little soluble in excess.	Same as dicodeine.	Same as dicodeine.
Caustic potash and solution of hydrochloride.	Oily precipitate if concentrated, becoming crystalline on standing; not markedly soluble in excess.	Oily precipitate if concentrated, not becoming crystalline; more dilute solutions give a white amorphous precipitate, soluble in large excess.	Same as dicodeine.	Same as dicodeine.

Reagent, &c.	Codeine.	Dicodeine.	Tricodeine.	Tetracodeine.
Action of hydrochloric acid not pushed to extreme.	Product contains Cl for C <sub>36</sub> ; further action contains Cl <sub>2</sub> for C <sub>36</sub> .	Product contains Cl for C <sub>72</sub> .	H <sub>2</sub> O removed for C <sub>18</sub> ; product contains no basic Cl.	Nil.
Action of hydriodic acid in conjunction with phosphorus.	Polymerises to tetra series, forming bases derived from (C <sub>17</sub> H <sub>21</sub> NO <sub>3</sub> ) <sub>8</sub> , or (C <sub>17</sub> H <sub>21</sub> NO <sub>2</sub> ) <sub>8</sub> ; H <sub>2</sub> being added on for C <sub>17</sub> in product, and CH <sub>3</sub> evolved for C <sub>18</sub> in original.	Polymerises to tetra series, forming bases derived from (C <sub>17</sub> H <sub>20</sub> NO <sub>3</sub> ) <sub>8</sub> , H being added on for C <sub>17</sub> in product, and CH <sub>3</sub> evolved for C <sub>18</sub> in original.	..	OH <sub>2</sub> removed, and HI added on (or I substituted for OH), no hydrogen added on; CH <sub>3</sub> removed for C <sub>18</sub> in original.
Action of sulphuric acid not pushed to extreme.	Polymerises, forming successively di-, tri-, and tetracodeine.	Polymerises, forming tetracodeine.	..	Nil; further action probably dehydrates and oxidizes.
Formula inferred from above properties and reactions.	C <sub>36</sub> H <sub>42</sub> N <sub>2</sub> O <sub>6</sub> .	C <sub>72</sub> H <sub>84</sub> N <sub>4</sub> O <sub>12</sub> .	C <sub>108</sub> H <sub>126</sub> N <sub>6</sub> O <sub>18</sub> .	C <sub>144</sub> H <sub>168</sub> N <sub>8</sub> O <sub>24</sub> .
Physiological action of 0.1 grm. of anhydrous hydrochloride, subcutaneously injected into adult cats.	Extreme hypersensitiveness and cerebral congestion; dilatation of pupils; no diarrhoea; no vomiting in any instance.	No hypersensitiveness nor cerebral congestion; dilatation of pupils; vomiting in every instance.  With a dog profuse diarrhoea, without vomiting.	Hypersensitive-ness scarcely marked; vomiting in some instances, in others salivation and defæcation.	No hypersensitiveness; vomiting, salivation, or diarrhoea in every case; great depression.  With a dog profuse salivation and depression.

C. R. A. W.

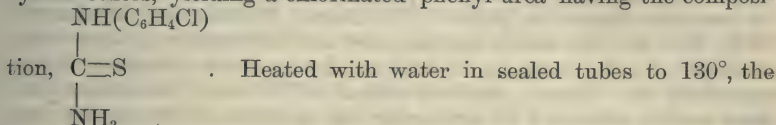
### Chlorinated and Iodated Phenylc Mustard Oil. By S. M. LOSANITSCH (Deut. Chem. Ges. Ber., iv, 156—158).

1. AN alcoholic solution of chloriniline, treated with bisulphide of carbon, gives, after proper purification, a urea, crystallising from alcohol in long, white needles, melting at 166°, and having the composition—

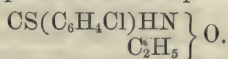




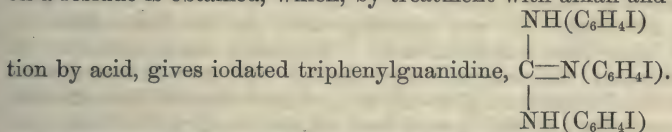
An alcoholic solution of this substance, treated with alcoholic iodine solution, yields chlorophenylic mustard oil or chlorophenyl isosulphocyanate,  $\left. \begin{smallmatrix} \text{C}_6\text{H}_4\text{Cl} \\ \text{CS} \end{smallmatrix} \right\}$ , in colourless needles, melting at  $40^\circ$ . This compound reacts with ammonia in the same manner as the other isosulphocyanic ethers, yielding a chlorinated phenyl-urea having the composition



chlorophenylic isosulphocyanate is resolved into carbon dioxide, hydrogen sulphide, and chloraniline. With absolute alcohol, on the other hand, it yields a semi-sulphuretted chlorophenyl-urethane—



2. Iodaniline behaves with carbon bisulphide similarly to chloraniline. In the formation of the corresponding iodated phenylic mustard oil a residue is obtained, which, by treatment with alkali and precipita-



A corresponding compound appears also to be formed in the preparation of the chlorophenylic mustard oil.

M. M. P. M.

**Action of Alkalis upon Lignite.** By L. SCHINNERER and T. MORAWSKI (Deut. Chem. Ges. Ber., v, 185, &c.).

On fusing lignite from Traunthal with three times its weight of caustic potash, pyrocatechin is formed; but this compound is not obtained if the lignite be previously exhausted with ether, which shows that it is formed from the bitumen of lignite. Pyrocatechin was also obtained from other lignites, but only from those which exhibit a distinct ligneous structure. Lignites of older formations do not yield pyrocatechin, and coal is not acted upon at all by fusing it with alkalis.

C. S.

**Tetronerythrin, a new Organic Colouring Matter.** By Dr. MIRM (Pogg. Ann., cxlv, 170—174).

THIS substance is obtained from the red spots over the eyes of the black-cock and pheasant; also from the reddish parts of the trout, the crab, and the fruit of *Phialopsis rubra*. The colouring matter is soluble in chloroform; unchanged by caustic potash; concentrated sulphuric acid turns it indigo-blue, then black. It is also soluble in carbon bisulphide and ether. It differs from the colouring matter of blood.

The author is engaged in investigating this substance.

M. M. P. M.

## Physiological Chemistry.

### The Quantity of Nitrogen in Muscular Tissue. By J. NOWAK (Wien. Akad. Ber., lxiv [2], 359—376).

AFTER commenting on the discrepancies in the percentage of nitrogen in muscular tissue, as given by W. Mayer, Playfair and Böckmann, Will, Voit, &c., the author inquires how such differences as 3 per cent., exhibited by the extremes of analyses by the above chemists, can be accounted for. Finding that the method of Will and Varrentrapp had been usually employed for estimating the amount of nitrogen, he was induced to test the accuracy of that method when applied to the nitrogenous constituents of the body not containing nitrogen oxides. Operating on uric and kynurenic acids, he found that both the method of Will and Varrentrapp, and that of Dumas yielded accurate and accordant results with uric acid; but that whilst the latter method yielded good results with kynurenic acid, Will's method yielded discordant figures, and the percentage of nitrogen found was much too low.

The muscular tissue employed for analysis was that of the horse, dog, ox, and man. It was carefully dried in the water-bath for 48 hours, then over sulphuric acid. Duplicate experiments in all cases gave results which agreed very closely. 100 parts of beef yielded 22·62—25·2; of horse-flesh 25·4—26·465; of dog's flesh 26·233—28·452; and of human flesh 20·434 (a very lean subject) to 23·806 of dry substance. A trace of ammonia was given off during the drying process. The dried flesh was analysed by both the above methods, several determinations being made and unusual precautions taken.

On comparing the results obtained by Will's method with those obtained by combustion with cupric oxide, it is manifest that the former method gives less nitrogen than the latter. Combustion with soda-lime does not drive off all the nitrogen in the form of ammonia. The discrepancies found in the two analyses of the same flesh made, according to Will's method, were sometimes as much as 0·8 per cent., whilst by Dumas's method the variation never exceeded 0·04 per cent. for dried flesh. The deficit of nitrogen by Will's method occasionally reached 3 per cent.

The percentage of nitrogen in the undried flesh was—

In the horse .....	3·506—4·020
„ dog .....	3·528—4·310
„ ox .....	3·443—3·780
„ man .....	3·238—3·802

In dry flesh—

In the horse .....	13·48—15·01
„ dog .....	12·40—16·43
„ ox .....	15·00—15·92
„ man .....	14·61—16·02

the analyses being made by Dumas's method.

**Analysis of Woman's Milk.** By A. SCHUKOFFSKY (Deut. Chem. Ges. Ber., v, 75—77).

THE author shows that most methods employed for the analysis of milk do not give correct results, especially in the case of woman's milk.

The casein of woman's milk differs from that of other milk in that it is not curdled thoroughly (if at all) by carbonic and acetic acids. The method of precipitating the casein by magnesium sulphate also gives unsatisfactory results.

The methods in use for the estimation of fat are also imperfect, *e.g.*, those in which gypsum or chalk is added to the milk, the resulting mixture dried, and the fat extracted by exhausting with ether; the presence of fat in the residue may be indicated by the microscope. Apparently the ether is prevented from acting on the fat by the casein envelopes which surround the globules.

Hoppe-Seyler has remedied this source of error by adding caustic potash to the milk, whereby the casein is decomposed. The potash however acts on the milk-sugar, forming decomposition-products, which dissolve in the ether together with the fat, and so vitiate the result.

When a sufficient quantity of ether is added to woman's milk, and the mixture is allowed to stand at rest for some days, two layers are formed—an upper one, thick and starch-like, and a lower, which is transparent. Strong alcohol (90—96 per cent.) added to this curdles it and precipitates the casein, whilst the fat floats on the top.

The author, having studied these reactions, recommends the following method for the estimation of fat in woman's milk:—20 c.c. of ether are added to 20 c.c. of the milk; the mixture is stirred, and to it 30 c.c. of strong alcohol are added. This mixture is allowed to stand for about 24 hours, in which time the milk-sugar separates in crystals on the sides of the vessel. The sugar and casein are filtered off and washed with anhydrous ether and strong alcohol; the filtrate and washings are evaporated on a water-bath till free from alcohol; and the residue is again treated with ether, then allowed to evaporate spontaneously, and finally dried at 100° and weighed.

C. C.

**Observations on some Instances of Colourless Bile.** By E. RITTER (Compt. rend., lxxiv, 813—815).

GALL bladders have often been found containing a colourless fluid, which has usually been regarded as mucus. The author has examined a number of cases of this kind in the human subject and in animals, and on analysis of the fluid finds that it contains salts of bile-acids with small quantities of mineral salts, fat, and cholesterin, and traces of other organic matters, but without colouring matter. Observations on the subject are not yet sufficiently numerous and are too incomplete to admit of a satisfactory explanation; but the author points out that in several cases, especially in animals, the colourless bile accompanied jaundice, and in all cases the liver presented a condition of fatty degeneration more or less advanced.

W. A. T.



### Artificial Conversion of Bilirubin into Urinary Colouring Matter. By R. MALY (Ann. Chem. Pharm., clxi, 368).

WHEN bilirubin is dissolved in dilute soda or potash ley, and sodium amalgam added, air being excluded, no hydrogen is evolved, but the dark colour gradually lightens; after two or three days' action the colour is yellow or bright brown-yellow and hydrogen is then evolved. Hydrochloric acid separates a pigment, which seems to be a weak acid; with alkalis it yields brown-yellow soluble salts, with heavy metals insoluble compounds separating in red flakes; it is readily soluble in alcohol, slightly in water, and readily in ammonia and alkalis, also in ether, liquid hydrocarbons, glacial acetic acid, and chloroform. Its spectrum has a characteristic dark black absorption-band, between the green and blue (Fraunhofer's lines, *b* to *F*); this is more marked in acid solution than in alkaline. The author considers that this product is identical with the urobilin of Jaffé (Virchow's *Archiv.*, 47) from normal and febrile urine; it also agrees with the product from excrement obtained by Vaulair and Masius (*Centralbl. f. d. Med. Wissensch.*, 1871, No. 24), and with the urinary colouring matter obtained by Scherer; it may be appropriately termed *hydrobilirubin*. It is not identical with choletelin, although Heinsius and Campbell have considered this to be the same as the colouring matter of urine and fæces.

Biliverdin seems to act with sodium amalgam in a similar manner.

C. R. A. W.

### On the Elimination of Alcohol. By A. DUPRÉ (Proc. Roy. Soc., vol. xx, p. 268).

IF, after several days' total abstinence, a certain quantity of alcohol be taken daily, and the amount of alcohol eliminated daily during the same time, by any one of the channels of elimination, be estimated, one of two things may happen. Firstly, the amount of alcohol eliminated per day may remain a constant quantity; or secondly, the amount eliminated may at first increase from day to day, and become constant only after a shorter or longer continuance of the alcohol diet. The first case would prove that the daily dose of alcohol is also disposed of daily, none remaining behind to augment the next day's elimination; the second case would show that the daily dose is not disposed of within the twenty-four hours, but that it requires several days to be either eliminated or otherwise disposed of. In either case the amount eliminated, after elimination has become constant, will give the fraction eliminated from one day's consumption.

Guided by these considerations, the author has made a series of experiments in which the alcohol eliminated in breath and urine was estimated, 1st, under a continued alcohol diet; 2nd, after a single dose of alcohol.

In the first series 584.236 grams of absolute alcohol were taken in the course of 12 days. The amount of alcohol in both breath and urine was—

On the 1st day .....	0.0572 gram.
„ 6th day .....	0.0497 „
„ 12th day .....	0.0340 „

In the second experiment 24·34 grams of alcohol were taken in a single dose; elimination ceased to be perceptible nine hours after the alcohol had been taken. The total amount eliminated in breath and urine was 0·3106 grm.

The result of both series of experiments has led the author to the following conclusions:—

First. The amount of alcohol eliminated per day does not increase with the continuance of the alcohol diet; therefore, all the alcohol consumed daily must, of necessity, be disposed of daily, and as it certainly is not eliminated within that time, it must be destroyed in the system.

Secondly. The elimination of alcohol following the taking of a dose, or doses, of alcohol is completed 24 hours after the last dose has been taken.

Thirdly. The amount of alcohol eliminated in both breath and urine is a minute fraction only of the alcohol taken.

In the course of these experiments the author found that a substance is normally contained in human urine which gives all the reactions usually employed for the detection of small quantities of alcohol. The nature of the substance, apparently not alcohol, could not, however, be determined, owing to the extremely minute quantity of it which is present in the urine.

A. D.

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### Examination of the Air in the Barracks at Aargau. By

T. SIMLER (Versuchs-Stationen Organ, xiv, 246—248).

THE largest chamber in the barracks had a capacity of 150,000 c. ft.; in this room 500 French prisoners slept. The air was examined when the room was empty, and again early in the morning before the soldiers had risen. In the first case, the air contained 5·38 vols. of carbonic acid, in the latter 39·09 vols., per 10,000. The number of men was then reduced to 300, upon which their health perceptibly improved.

R. W.

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## Chemistry of Vegetable Physiology and Agriculture.

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### Formation of Ozone by Plants. By C. BELLUCCI (Gazzetta

Chimica Italiana, i, 687—690).

SCOUTETTEN, Bineau, Kosmann, and de Luca, instituted experiments from the results of which they inferred that plants are sources of ozone, whilst Cloez (*Ann. Chim. Phys.* 1856) on the contrary showed conclusively that the apparent presence of ozone was due to other causes. He passed the aëriform products from the plants through two tubes placed side by side, and containing iodised test-paper; one of these was exposed to the action of light, and the test-paper became coloured, whilst in the other which was protected from the light, it

remained unaltered, showing that the action was due, not to ozone evolved from the plants, but to the effects of moisture, oxygen, and light on the test-paper. The author has carefully repeated the experiments of Cloez, and devised new ones, in which he introduced into a large Woulfe's bottle containing water saturated with carbonic anhydride, and to which a small quantity of potassium iodide and starch was added, sprigs and leaves of the following plants: *Taxus baccata*, *Juniperus virginiana*, *Abies vulgaris*, *Thuja orientalis*, *Prunus Laurocerasus*, *Buxus sempervirens*, and *Chara foetida*. The apparatus was then placed in bright sunshine, but no change was observable in the liquid, proving that the green parts of plants do not evolve ozone under the influence of the solar rays.

C. E. G.

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**Formation of Asparagine in Vetches.** By A. COSSA (Gazzetta Chimica Italiana, i, 683—685).

PIRIA found asparagine in vetches which had been grown exposed to bright light, as well as in those grown in darkness. Some years after Pasteur (*Ann. Chim. Phys.*, 1857) grew a large quantity of vetches in the garden of the Academy at Strasburg, but did not obtain a trace of asparagine from 200 litres of the sap, whilst he found abundance in vetches grown in the same soil in a cellar. The author, therefore, grew some vetches in the month of July, and from a kilogram of those which had been exposed to light, he obtained 16.25 grams of pure asparagine, and from an equal weight of those grown in a cellar, he obtained 13.50 grams, the asparagine being proved to be identical in both cases; similar results were obtained in the months of August and September.

Piria's want of success probably arose from the circumstance that the sap of vetches, especially when grown exposed to light, readily ferments, the asparagine being decomposed and ammonium succinate being formed.

C. E. G.

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**Origin of the Chemical Work in the Production of Organic Matter in Chlorophyll-cells.** By A. MEYER (Versuchs-Stationen Organ, xiv, 176—179).

THIS is a reply to a statement by W. Köppen, that the axioms laid down by Clausius with regard to the mechanical theory of heat, are insufficient to explain the operations of plant growth.

R. W.

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**The Mineral Constituents of Wheat-grain from the Development of the Ovary until over-ripe.** By R. HEINRICH (*Ann. der Landwirtschaft*, 1871, 31—50).

THESE experiments were undertaken in order to ascertain the possible functions of the mineral matters in plants, and to determine the relations existing between their organic and inorganic constituents.



The grain was the part of the plant chosen for examination, as constituting the youngest and upper portions; it is least likely to contain any excess of mineral matter beyond that required for its normal development, and so in it the ratios between the organic and inorganic constituents can be better ascertained. The grain was analysed at five different stages of development: 1st. The ovaries were collected whilst the wheat was still in flower. 2nd. Fourteen days later. 3rd. After another 14 days, when the wheat began to ripen. 4th. Seven days later, when the wheat was ripe and cut. 5th. Fourteen days after harvest, when over-ripe. The results obtained show that the potash remained throughout this time in a nearly fixed ratio to the dextrin and gummy matters, the lime to the cellulose, and the phosphoric acid to the albuminoids; the ratios were—

- 1 Potash to 10—11 Gummy matters.
- 1 Lime to 41—43 Cellulose.
- 1 Phosphoric acid to 1·8—2 Nitrogen.

The starch had no fixed ratio to any of the mineral matters, but continued to increase relatively to them all, throughout the whole time.

The author dwells principally on the ratio existing between the lime and the cellulose. The experiments of Payen and others show that although the young cell-membranes which are soft contain no ash-constituents, yet the older cell-walls contain a considerable quantity of lime which cannot be altogether removed by dilute acids. Also in the experiments of Hellriegel, in which plants were grown without lime by water-culture, the plants were without their normal firmness and stiffness. From these considerations it is suggested that the lime not only has a settled relation to the cellulose, but is necessary also to the normal hardness and stiffness of plants. The "lodging" of corn, produced by high farming, is due to a deficiency of stiffness in the straw, and was formerly thought to proceed from a want of silica in an available form in the soil. But this theory is completely confuted by the water-culture experiments of Sachs and others, in which no silica was supplied, and yet the normal stiffness of the stalk was secured; also by the fact that the straw of lodged corn contains just as much silica as that of unlodged.

But the parts of plants which are distinguished by special hardness are rich in lime; thus the internodes of the wheat-stem contain in 1,000 parts 1·78 of lime, and the harder nodes 4·73 of lime.

Again, the ash of spring wood is much poorer in lime than that of autumn wood; in the case of walnut, Richardson found 22 per cent. of lime in the ash of the spring wood, and 55 per cent. in the ash of the autumn wood. In consequence of these results, the author proposes, as a remedy for lodging, the employment of an artificial supply of lime in some readily available form, such as finely powdered chalk or gypsum, or dilute solution of calcium chloride, at the same time making use of thinner seeding, so that the lower parts of the plant may be exposed to sunlight, and the circulation of air facilitated.

**Influence of River and Spring Water on Meadow-Grass.** By A. BEYER (Ann. der Landwirtschaft, 1871, 165—170).

A MIXTURE of common meadow-grass seeds was sown in pure quartz sand contained in boxes so arranged that water could trickle through them in imitation of water-meadows.

The experiments continued over three years, one box being kept watered with river water,\* and another with spring water.

The first year no crop was obtained. The grasses did not flower in the second year, but tillered towards the end of the summer.

During the third summer in the box watered with river-water, *Holcus lanatus* was almost exclusively developed, and the plants flowered and ripened, whilst in that watered with spring-water, the plants were in a great measure green.

In the autumn the roots in the former were examined and found largely developed. In the last two years a total quantity of 20·067 grams of dry grass was obtained from a surface of 6 inches square, derived from ·3 gram of seeds.

An experiment was also tried with an almost sterile soil, from which the finer particles had been washed out; this was kept moistened with distilled water. The seeds germinated well, and were vigorous during the first two summers, but refused to grow after.

From the results obtained the author concludes—

1. That meadow-grasses can come to full development by means of the food contained in spring or river-water, as represented by Vincent.

2. That during the first period of growth from such dilute solutions, the food is devoted to the formation of roots, and that only after a large root-surface has been formed, can the organs above the surface obtain sufficient nourishment to arrive at maturity.

3. That the quality of the water has a separate and distinct influence on the total produce and on the development of different grasses in the same mixture of seeds. With river-water, *Holcus lanatus* became developed in the mixture of grass-seed in a greatly preponderating proportion, whereas with spring-water few plants of *Holcus lanatus* developed; but the produce of the mixed meadow-grasses was greater.

4. That an apparently totally barren soil with proper irrigation can grow grasses for a short time.

E. K.

**Experiments on Sugar-Beet.** By A. H. CHURCH (Trans. High. Agri. Soc. [4], iv, 85—92).

A CROP of white beet was grown in 1870, on the oolitic clay of the forest-marble; no manure was used, nor had any been applied to the soil since 1866. The seed was sown in April. From the beginning of August the character of the crop was determined fortnightly, with the following results:—

\* This is called rain water (Regenwasser), but from the analysis given was evidently a river water.—E. K.

Beet taken up.	Leaf to 100 root.	Sugar per cent.	During the preceding fortnight.		
			Mean temperature F°.	Rain (inches).	Increase of sugar.
August 10 .....	153	8·70	65°	·743	—
„ 24 .....	126	9·20	61°	1·630	·50
September 7 .....	102	9·77	57°	1·180	·57
„ 21 .....	91	10·48	55°	·485	·71
October 5 .....	85	12·00	56°	None	1·52
„ 19 .....	65	13·18	49°	2·494	1·18
November 2 .....	65	13·47	49°	1·663	·29
„ 16 .....	[58]	[13·53]	43°	·210	·06
„ 30 .....	52	13·58	43°	1·723	·05
December 28 .....	—	10·70	—	—	—
January 31.....	—	10·55	—	—	—

The roots, on November 2, averaged  $1\frac{1}{2}$  lb.: being planted at the rate of 56,000 per acre, the yield was (by calculation)  $37\frac{1}{2}$  tons. Beet-roots which run to seed in the autumn, contain about one-fifth less sugar than normal roots.

R. W.

### Constituents of Yellow-Lupine Seed. By A. BEYER (Versuchs-Stationen Organ, xiv, 161—176).

A SECTION of the moist seed is strongly acid to litmus-paper. The author conclusively establishes the presence of citric acid. According to Ritthausen, malic and oxalic acids are present.

Another ingredient is a viscid substance, soluble in alcohol; this the author did not succeed in obtaining pure.

The seed contains two fats—a fluid fat extracted by cold ether; and a solid fat, obtained by treatment with hot alcohol after the extraction by ether. When purified, the percentage composition of the fluid fat is 75·7 C., 11·35 H., ·098 P., 12·852 O.; while that of the solid fat is 72·68 C., 10·84 H., 1·56 P., 14·92 O. The amount of phosphorus in the solid fat is remarkable: it was quite free from adhering phosphates. Knop found 1·25 per cent. of phosphorus in a fat from a sugar-pea.

The alkaloids of lupine-seed are best extracted by means of alcohol containing hydrochloric acid; when isolated they are found to be fluid bodies resembling conine. The author separates the alkaloids by the different solubility of their platinum salts. The platinum salt insoluble in alcohol and in cold water, has the formula  $C_{17}H_{38}N_2O_2Cl_2.PtCl_4$ ; the more soluble platinum salt has the formula  $C_{20}H_{46}N_2O_4Cl_2.PtCl_4$ . The soluble platinum salt corresponds to an alkaloid soluble in water, and *vice versa*.

Siewert has separated the two alkaloids by distillation. The one distilling at  $216^\circ$  corresponds to the insoluble platinum salt; that distilling at  $261^\circ$  to the soluble. Siewert's formulæ for the alkaloids are in each case less, by a molecule of water, than those deduced from the above platinum salts.

R. W.



**Investigations on the Seeds of the Brassicæ.** By J. SCHROEDER  
(Versuchs-Stationen Organ, xiv, 179—194).

THE author endeavours to determine those physical characteristics of the seeds in question, which would afford the means of identifying the seeds present in any given sample. Among seeds of the same description, both colour and size vary. In the following table the average weight in grams of 1,000 seeds, and the weight of 1,000 of the heaviest and lightest seeds, are given:—

Description of seed.	Average.	Heaviest.	Lightest.
<i>Br. oleracea atrorubens</i> .....	4·417	5·850	3·330
<i>Br. oleracea germanorum</i> (white cabbage) ....	4·267	5·690	3·040
<i>Br. oleracea elliptica</i> .....	3·987	5·770	3·010
<i>Br. oleracea protojodusa</i> (English blue Kohlrabi) .....	3·971	5·490	2·540
<i>Br. oleracea caulorapa</i> (white Kohlrabi).....	3·349	5·350	2·500
<i>Br. oleracea praeox</i> (Savoy) .....	3·794	5·450	2·320
<i>Br. oleracea bullata</i> „ .....	2·630	4·670	2·070
<i>Br. oleracea Loudoni</i> (brocoli) .....	3·600	5·390	2·450
<i>Br. oleracea cauliflower</i> .....	3·534	5·430	2·530
<i>Br. oleracea gemmifera</i> (Brussels sprouts) ....	3·108	4·670	2·210
<i>Br. oleracea selenisia</i> .....	3·015	4·360	1·710
<i>Br. oleracea sabellica</i> .....	2·900	4·430	1·970
<i>Br. napus hyemalis</i> (winter rape) .....	4·667	6·320	3·000
<i>Br. napus annua</i> (summer rape) .....	1·901	2·460	1·390
<i>Br. rapa leucopyrgus</i> (white turnip) .....	2·268	3·170	1·650
<i>Br. rapa leucoplax</i> „ .....	2·146	3·050	1·430
<i>Br. rapa biennis</i> (stubble turnip) .....	2·142	2·820	1·470
<i>Br. rapa Teltoviensis</i> (yellow turnip) .....	1·141	1·750	·920
<i>Br. nigra vulgaris</i> (a variety of cabbage).....	1·326	1·900	1·030

In most cases a rather larger proportion of the heavier seeds germinated than of the lighter ones, but this was not universal.

It was found possible to discriminate the seeds to some extent by means of a microscopic examination of the sections of their shells; the characteristic structure was in all cases towards the exterior of the shell. All the varieties of *Brassica oleracea* form one group, *Brassica napus* and *rapa* a second group, and *Brassica nigra* a third group, on this system of classification. Woodcuts of the three characteristic sections are given.

R. W.

**Valuation of Commercial Feeding Stuffs.** By H. SCHULTZE  
(Ann. der Landwirtschaft, 1871, 347—356).

By affixing money values to the effective constituents of feeding materials, their different digestibility in distinct classes of food being taken into account, the author endeavours to arrive at the comparative value of feeding stuffs. Our knowledge of the digestibility of the various constituents of food is still scanty. The author allows for the albuminoids, fat or oil and soluble carbohydrates in corn, roots and their products the prices originally suggested by Grouven. In oil-cakes 75 per

cent. of the albuminoids and the whole of the other constituents are reckoned effective.

In green foods 62·5 per cent., and in hay and straw 50 per cent. of the albuminoids. In these last two classes only 40 per cent. of the oil is allowed as serviceable, since chlorophyll and resin are included with it in analysis; the full value is affixed to the other carbohydrates.

A list of the money values of the principal commercial feeding stuffs thus estimated is given, by comparing which with the market price, it is thought that the agriculturist may be enabled to find in what form he can purchase the desired food most advantageously. Satisfactory results will only be obtained when foods of a similar nature are compared.

E. K.

### Humus-substances of the Soil. By W. DETMER (Versuchs-Stationen Organ, xiv, 248—300).

THE humic acid obtained by Mulder contained 3—5 per cent. of nitrogen; the author endeavoured to prepare a purer substance. Peat, and various kinds of peaty soil, were extracted with solution of potassium carbonate, the solution precipitated by hydrochloric acid, and the precipitate subjected to a great number of purifying processes. The humic acid was finally precipitated from its solution in boiling water by the addition of hydrochloric acid; it then contained only 1·79 per cent. of nitrogen. The nitrogen present in the earlier stages of purification did not exist as ammonia. The purified humic acid, dried at 120°, gave a mean percentage of 59·75 C., 4·61 H., agreeing with the formula  $C_{20}H_{18}O_9$ ; the composition of the salts shows, however, that the true formula is  $C_{60}H_{54}O_{27}$ .

Humic acid is amorphous. It begins to decompose at 145°. When undried, it dissolves in 8333 parts of water at 6°, and in 625 parts at 100°; after drying it requires 13784 parts of boiling water for solution. The presence of salts diminishes its solubility. It is more soluble in phosphoric acid than in other acids. Humic acid reddens litmus; it expels carbonic acid from metallic carbonates, forming insoluble compounds, save with alkalis. Its solution in ammonia leaves, when dried, a substance having the formula  $C_{60}H_{48}(NH_4)_6O_{27}$ , which is soluble in 2·2 pts. of water. Metallic salts occasion precipitates in ammonium humate. The precipitate by calcium chloride has the formula  $C_{60}H_{46}Ca_3(NH_4)_2O_{27}$ ; that by ferric chloride has the formula  $C_{60}H_{46}(Fe_2)^{vi}(NH_4)_2O_{27}$ ; the precipitate by silver nitrate is  $C_{60}H_{46}Ag_3O_{27}$ . All these compounds are amorphous.

The acid prepared from brown peat (called ulmic acid by Mulder) is identical in composition and properties with that obtained from black peat. Humin, the insoluble humus-substance, is difficult to obtain free from undecomposed vegetable fibre. Crenic and apocrenic acids appear to be products of the oxidation of humic acid.

The changes which peat undergoes during its formation are shown by the following analyses of samples from Nienwalder Moor. The samples were dried at 120°:—

Description of peat.	Ash per cent.	Composition of organic substance per cent.			
		N.	C.	H.	O.
Brown peat, from surface.....	2·719	·80	57·75	5·43	36·02
Nearly black peat, at 7 feet.....	7·423	2·10	62·02	5·21	30·67
Black peat, at 14 feet .....	9·164	4·05	64·07	5·01	26·87

The amount of humus in a soil is best ascertained by oxidation with potassium bichromate, and estimation of the carbonic acid evolved. A moderate quantity of humus improves soil in many ways. From its dark colour humus is a good absorbent of heat; its specific heat is much above that of soil; it is a hygroscopic substance, and greatly increases the water-holding power of sandy soils; it has the power of absorbing ammonia; by its decomposition it is a source of carbonic acid; the mechanical condition of most soils is improved by its presence. When, however, humus is present in excessive quantity, it acts injuriously, by deoxidising ferric salts, and in other ways. Experimental data are given for most of these statements.

Humic acid is a strictly colloïd body, and cannot, therefore, directly serve for the nourishment of plants.

R. W.

### Water-holding Power of Soil and Soil-constituents. By

C. TREUTLER (Versuchs-Stationen Organ, xiv, 301—307).

100 PARTS of each of the following substances retained, after draining 24 hours in a funnel, the following amounts of water:—Fine soil, 68·2; quartz sand, 28; powdered chalk, 50; quicklime, 122; magnesia, 460; bone-meal, 92. The experiment with magnesia lasted 2—3 days. Mixtures of these substances retained somewhat *less* water than was calculated from the absorbing power of their ingredients. Soil mixed with quicklime retained, however, rather more than the calculated amount of water.

R. W.

### Composition of Farmyard-manure. By T. ANDERSON (Trans. High. Agri. Soc. [4], iv, 321).

SAMPLES of farmyard-manure from eight superior farms in Scotland were analysed. The following table shows the mean composition, and the highest and lowest percentages found:—



	Mean.	Highest.	Lowest.
Water .....	72·48	83·02	58·64
Organic matter.....	13·94	21·68	7·24
Potash .....	·32	·60	·10
Soda .....	·16	·39	·07
Lime .....	·59	·95	·30
Magnesia .....	·02	·12	traces
Phosphoric acid .....	·31	·62	·09
Sulphuric acid .....	·12	·15	·06
Carbonic acid and chlorine .....	·52	—	—
Ferrie oxide and alumina .....	·45	·83	traces
Sand .....	11·09	18·36	3·74
	100·00		
Nitrogen .....	·38	·49	·19

R. W.

*On the Sources of the Salts of Potash and their Use as Manures.* By T. ANDERSON (Trans. High. Agri. Soc., [4], iv, 303—317).

### Composition and Agricultural Value of Earth-Closet Manure.

By A. VOELCKER (Jour. Roy. Agri. Soc. [2], viii, 185—203).

MOULE'S earth-closets are efficient in a sanitary point of view; they are specially adapted for use in villages. Dry, sifted earth is employed to cover the deposit. After a time the whole is mixed, and, when dry, is used again. Earth containing clay may be used five times over. Analyses of the manure obtained at Wakefield prison showed that the nitrogen in the dry soil increased by ·066 per cent., and the phosphoric acid by ·11 per cent., each time the soil was made use of. In a trial made by Dr. Gilbert, the nitrogen increased by ·155 per cent. Calculation also shows the low value of such manure. Reckoning the excreta of one person as worth 9s. per annum, and supposing (according to Mr. Moule) that 1 ton of earth will serve  $2\frac{1}{2}$  persons for a year, the value of a ton could not exceed 22s. 6d.; but as the greater part of the urine will not be collected, the money value will probably be only one-third of this, or 7s. 6d.

R. W.

## Analytical Chemistry.

**Further Observations on the Estimation of Chlorine by Ammonio-ferrous Sulphate.** By E. BILTZ (Arch. Pharm. [2], xcix, 97—106).

Soon after the publication of the author's first paper on this subject, a statement was made in the *Pharm. Zeitung*, No. 43, that more satis-

factory results could be obtained by this method by heating the solutions prior to the addition of permanganate. The author, however, has found that even then the results are less exact than when, as he proposed, the solution of the double salt is strongly acidified before the addition of chlorine water. The author has further observed that if chlorine-water be added in sufficient quantity to oxidize the whole of the ferrous oxide present, some remains unoxidized, whilst hypochlorous acid is formed. He considers, therefore, that the double salt is valueless for the determination of chlorine.

A. T.

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**Sodium Sulphide as a Blow-pipe Reagent.** By JEAN (Dingl. Polyt. J., cciii, 242).

THE body to be examined is fused with borax in the inner flame; sodium sulphide is added to the bead, which is again heated in the same flame. Iron, lead, bismuth, nickel, cobalt, palladium, thallium, silver, copper, uranium, &c., give a brown or black opaque mass; zinc a white opaque bead; cadmium a scarlet-red bead when hot, yellow when cold; manganese dirty chestnut-brown; gold and platinum a clear transparent mahogany-coloured mass; zinc a transparent yellowish-brown one; chromium gives green; arsenic and antimony a colourless clear mass; and vanadium and iridium a blood-red bead.

C. H. G.

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**The Spectra of Manganese in Blowpipe Beads.** By CHARLES HORNER (Chem. News, xxv, 139).

VERY small quantities of manganese, contained in blowpipe-beads, may be readily detected by examining the latter with the micro-spectroscope. The beads are prepared by fusing a trace of oxide with a small quantity of potassium chlorate in a platinum loop, the heat being carefully adjusted so that a pink and not a greenish-coloured bead is obtained. The pink bead, when strongly illuminated and examined with the spectrum microscope, exhibits three well-defined absorption-bands, lying between D and b, the bands being more or less distinct, according to the quantity of manganese present.

The green bead gives a somewhat less definite spectrum, consisting of two bands, one broad band covering the sodium line, and a very narrow band in the orange ray. The traces of manganese contained in minerals may be readily detected in this manner, even when the colour of the bead is disguised by the presence of other substances.

J. W.

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**Estimation of Combined Carbonic Acid in Water.** By EDWARD NICHOLSON (Chem. News, xxv, 137).

THE subject matter of this paper relates almost entirely to the practical working of a process devised by M. Lory, for the estimation of carbonates in potable waters, respecting which the author adduces evidence showing that it is perfectly worthless as a quantitative method.

The process, which is rather an extraordinary one, is quoted from Dr. Parke's "Manual of Hygiene;" it consists essentially in the employment of an acid solution of copper phosphate (or any similar compound, soluble in hydrochloric acid, without decomposition), which, having been standardised against a solution of sodium carbonate, is afterwards added to the water to be tested in such quantity that the precipitate which first appears is exactly redissolved. From the volume of solution consumed, the proportion of alkaline or earthy carbonate is calculated.

It is obvious that the precipitation of the phosphate by an alkaline solution, and the subsequent re-solution of the precipitate, depend entirely upon the acidity of the original solution, and not in any way upon the proportion of carbonates present; it is, therefore, liable to great variation in this respect; and since any solution possessing an alkaline reaction gives a similar indication, whether it contains caustic alkali, a carbonate, silicate, phosphate, or borate, the process on the whole must be considered objectionable, it being likely to lead the analyst to positively erroneous results.

The author does not offer any modification or improvement upon the methods which are usually adopted for the estimation of combined carbonic acid in waters.

J. W.

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### **The State of Combination of Silicic and Carbonic Acids in Water.** By EDWARD NICHOLSON (Chem. News, cxxv, 171).

THE amount of silicic acid and alumina contained in potable waters is generally so small, that in the statement of analyses where a formula is given for the saline combinations considered to be present, it is usual to leave silica and alumina uncombined. The author takes objection to this plan of tabulating the results, more especially as he finds that in the waters of India, silicic acid is by no means an insignificant constituent; and he has, therefore, endeavoured to ascertain the most probable combinations in which these compounds are contained in waters.

In order to show that silicic acid does not exist in water in an uncombined state, a sample containing as much as 8 centigrams per litre, was submitted to dialysis, from which 98 per cent. of silicic acid passed through the dialyser. This was considered sufficient proof that the silica must have been present in the form of soluble silicate. The conditions and properties of this silicate were afterwards ascertained by partially evaporating given quantities of the water, both in open and in closed vessels, and by submitting the solution as well as the deposit which occurred, to frequent analysis. It was found that after concentrating the water to one-half of its original bulk, 98.0 per cent. of the silica still remained in solution, but that when the evaporation was carried to dryness, the residue gently ignited, and treated with boiling water, 9.0 per cent. only of the silica passed into solution; and generally, that in waters containing both alkaline and earthy salts, provided atmospheric carbonic acid be excluded, the ratio of silicic acid



deposited to that which remained in solution, depended materially upon the extent to which the evaporation was carried.

It would appear that the alkaline, earthy, and aluminous silicates differ considerably in solubility; the aluminous silicate being the least soluble is deposited when the water has been concentrated to about one-half; magnesium silicate is deposited only towards the end of the evaporation, while sodium silicate being perfectly soluble remains in solution to the last.

The sodium silicate, however, is liable to be decomposed by atmospheric carbonic acid, which eliminates the silicic acid slowly during evaporation; and, further, when the residue is ignited in presence of calcium carbonate, nearly the whole of the silica combines with the calcium, forming insoluble calcium silicate.

The author does not, after all, give any very definite rules by which the combinations of silicic acid with aluminium, magnesium, and sodium may be adjusted; on the contrary, it appears to be distributed among them in a somewhat arbitrary manner. He would seem to imply, however, that after a water has been concentrated to about one-half of its bulk, and the deposit analysed, if silicic acid be found in presence of aluminium and magnesium, the quantity so found may be considered to be in combination with these bases, while any excess of silica subsequently obtained is to be reckoned as alkaline silicate.

J. W.

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### **Modification of Dumas' Method for the Estimation of Nitrogen in Organic Bodies.** By L. KESSLER (Compt. rend., lxxiv, 683).

THE combustion of the organic substance by means of oxide of copper, is conducted in the usual manner, but the gases produced are not directly collected in a graduated cylinder, but are received in a small caoutchouc bag, the latter being placed between the combustion-tube and the cylinder in which the gas is to be finally measured.

Before attaching the bag to the combustion-tube, some caustic soda solution is poured into it in order to absorb the carbonic anhydride; and during the combustion the whole absorption-apparatus is kept below the surface of water to prevent possible loss of gas by transfusion. When the operation is complete, the bag is emptied under water, and the contents collected and measured in the graduated glass jar.

J. W.

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### **Detection and Estimation of Paraffin in Stearin Candles.**

By M. HOCK (Dingl. Polyt. J., cciii, 313—315).

MAKERS of stearin candles mix paraffin with the fatty mass in quantities up to 20 per cent. Paraffin candle makers also mix stearic acid with their paraffin and attribute valuable properties to such a mixture, as far as candle-making is concerned. The attempt to determine if paraffin be present, and if so, to get some approximate idea of the quantity, in a sample of stearin and *vice versâ*, by means of the comparison of the melting point and specific gravity of such a mixture is shown to be useless, as these vary according to the source from which the paraffin is

obtained, as also in the case of the stearic acid, since the pure commercial article is by no means a chemically pure article.

A good method for detecting the presence of stearic acid in paraffin has been devised by R. Wagner, viz., by treating a boiling solution of the paraffin in alcohol with an alcoholic solution of neutral lead acetate, when, if stearic acid be present, a dense floccular precipitate appears, but none if it be absent. The best method, and one which can be used quantitatively as well as qualitatively, is described as follows:—Not less than five grams of the candle are taken and treated with warm solution of potassium hydrate, which must not be too concentrated. A soap is formed with the stearic acid, whilst the paraffin is left unaltered. Sodium chloride is thrown into the solution, whereby the soap is separated out as a soda soap, and in precipitating takes down the paraffin with it. The soap obtained is thrown on the filter and washed with cold water or very dilute spirits of wine. Thus, firstly, the sodium chloride is washed out, and finally, the soap is brought into solution and likewise washed through the filter, leaving the paraffin, which is then dried at a temperature below 35° C. so as not to fuse it. The paraffin is then treated on the filter with ether, and after repeated washing with this solvent, the ethereal solution is carefully evaporated in a weighed porcelain crucible, in the water-bath, at a low temperature. The residue consisting of the paraffin is then weighed, and the stearic acid is estimated by difference.

W. S.

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**On Colour Estimation.** By C. STAMMER (Dingl. Polyt. J., cciii, 137).

THE instrument described is a cheaper and improved form of the chromoscope, invented by the author. For use in sugar factories it is provided with a set of coloured glasses, to be used as colour-standards with which to compare the various products of the factory when brought into solutions of the same degree of sugar-contents.

C. H. G.

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**A New Colorimeter.** By SALLERON (Dingl. Polyt. J., cciii, 141).

THIS consists essentially of two glass troughs, with parallel sides placed edge to edge. The standard colour, in solution, is placed in one and the sample to be tested in the other. Light is thrown through both from a mirror and then water is added to the darker of the two, from a burette, till equality of tint is obtained. The apparatus is mounted on a suitable casing and stand. A woodcut is given.

C. H. G.

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**Method of quickly drying Flasks, &c., and adapting Wide to Narrow Tubes.** By G. ZETTNOW (Pogg. Ann., cxlv, 170).

1. Simply wash out the flask with alcohol, then with ether, and blow in air while heating.
2. Draw out the wider tube till it is of the same diameter as the narrower one.

M. M. P. M.

**A simple Quicksilver Lute.** By H. KARSTEN (Deut. Chem. Ges. Ber., v, 282).

IN cases where tubes cannot be connected by india-rubber, corks, &c., the author makes a gas-tight junction by making the two tubes to be joined vertical, the lower one capable of sliding within the other; when in this position the open end of the upper or outer tube is surrounded by mercury retained by a cup, through the bottom of which the smaller tube passes. The whole apparatus is most easily constructed, and can readily be taken to pieces and put together again.

C. R. A. W.

## Technical Chemistry.

**Mixing of Hydraulic Lime.** By V. WARTHA (Dingl. Polyt. J., ccii, 527—532).

IT was found that mixing even 15 per cent. of nearly pure unslaked lime with a natural hydraulic lime, made from a somewhat silicious marl, did not in any way interfere with the hardening power of the latter, but that when it was attempted to substitute ferruginous silicious lime, the mass, after binding, fell to powder when immersed in water. The explanation of this curious fact is found in the circumstance that the slaking of the impure, dead-burnt lime does not take place till after the cement has set, and that the consequent swelling causes the mass to break up.

C. H. G.

**Observations and Experiments on the Origin of the Hydraulic Powers of Mortars and Cements.** By F. KNAPP (Dingl. Polyt. J., ccii, 513—527).

DR. KNAPP discusses this question by the light of experiments published by Schott and others, and shows that the hydraulic properties of a cement depend as much, or more, on its mechanical state as on its chemical composition. Schott has shown that the coarse sandy parts of Portland cement are possessed of very slight powers of hardening under water, but if they be rubbed to a fine meal the resulting powder has all the properties of the original fine cement. From this and other parallel facts it is concluded that a cement (when dry or only just mixed with water) must have a great number of points of contact between its particles, so that when the hydration takes place they should become, as it were, grown together.

C. H. G.

**Talmi-gold.** By CLEMENS WINKLER (Ding. Polyt. J., cciii, 294—302).

AS the result of the great competition in the gilded jewellery manufacture, the prices have been pressed down lower and lower, and consequently the quality of the articles has suffered in a somewhat similar



ratio, until at length in Paris, Vienna, and other towns, articles are being freely sold as gilded, gold-plated, or as composed of a newly discovered species of gold (talmi-gold), which in fact contain little more than a trace of the true noble metal, generally as a thin plating, either of the pure metal or more usually of an alloy containing from 0.05 to 0.97 per cent. thereof, and frequently none at all. This talmi-gold was first used in Paris for the manufacture of ornamental wares, trinkets, &c., and these articles possessed great beauty and durability. The material for the preparation of the talmi-gold articles is obtained by rolling out gold-plated copper, pinchbeck, or brass plates, or drawing out to wire, in which processes the underlying copper, pinchbeck, &c., still retain their gold covering, which not only possesses remarkable strength, but is also more intimately united with these underlying metals, adheres more closely, and has not the porosity of the layer deposited in electro-gilding. The amount of gold contained in talmi-gold used in plating other metals or alloys seldom exceeds 1 per cent., and yet this offers great resistance to atmospheric action, sulphurous vapours, &c. The following is the result of the analysis of a portion of a talmi-gold chain, which for four years had been worn constantly without the least deterioration by tarnishing, &c.:—Copper, 89.88 per cent.; zinc, 9.32 (overlaid portion); gold, 1.03 (contained as gilt covering). On treatment with nitric acid, the central portion was dissolved, leaving the gilt covering in thin, partially corroded tubes.

W. S.

**Occurrence of Copper in Cajuput Oil.** By EDWARD HISTED  
(Pharm. J. Trans. [3], ii, 804).

THE presence of copper in cajuput oil was first observed by Guibourt, who found, on the examination of a certain specimen, as much as 0.0274 per cent.; at the present day, however, the actual occurrence of copper in well-authenticated samples of oil has been much doubted, more especially since the investigations of later chemists, have, as a rule, failed to corroborate the experiments of Guibourt.

The author having had placed at his disposal several samples of oil, the origin of which could be distinctly traced, submitted them, together with others obtained from commercial sources, to careful examination, and succeeded in obtaining, in every instance without distinction, abundant indications of the presence of copper.

It appears that cajuput oil, though naturally possessing a green colour, becomes perfectly colourless when redistilled. This colourless oil acts readily upon metallic copper, and in a few days re-acquires a green colour; the quantity of copper dissolved is, however, too small to render the oil unfit for medicinal use.

J. W.

**On the Action of Bone Charcoal in Sugar-making.** By C.  
WERNEKINCK (Dingl. Polyt. J., cciii, 60—66).

THE author, starting from previously known facts, frames an hypothesis to account for the action of animal charcoal in decolorising

vegetable solutions and in absorbing lime from a solution of sugar-lime. He connects the undoubted fact that such charcoal absorbs and condenses large quantities of the atmospheric gases with the powers named, by assuming that the decolorising power is due to the oxidising power of condensed oxygen, and the lime-absorbing action to the carbonic acid contained in the pores. He does not quote any experiments in support of his view.

C. H. G.

[The abstractor can state that animal charcoal deprived of its gases by heating to redness in a Sprengel vacuum, is capable of decolorising a solution deprived of dissolved air (and retained *in vacuo*) as perfectly as the ordinary material.]

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**Method of Separating Oxide of Iron from Raw Sugar.** (Dingl. Polyt. J., cciii, 325.)

MESSRS. Drummond and Sterry Hunt have lately taken out a patent for the above purpose. The method is briefly as follows:—To the solution of sugar, milk of lime is added till it becomes faintly alkaline. Then barium- or calcium-sulphide is added in powder, but preferably in solution; and the whole is well stirred up whilst it is heated to a temperature between 38° and 65° C. If now the solution communicates a dark shade to a piece of paper moistened with lead acetate, the quantity of sulphide added is sufficient, if not, more is added. A solution of magnesium sulphate is next added, 1½ pounds of this salt being used for every pound of barium sulphide or half pound of calcium sulphide employed. The whole is well stirred and heated. A small addition of blood or white of egg accelerates the subsequent filtration, when the sugar is ready for the refining process. In most cases two or three pounds of barium sulphide or half as much calcium sulphide, are sufficient for the ton of sugar. In the process described, the iron which is contained in the sugar solution as oxide, is precipitated as sulphide, and the excess of barium (or calcium) sulphide employed, is removed by the magnesium sulphate subsequently added, a very unstable magnesium sulphide remaining.

The mixed oxide of iron and barium (or calcium) sulphate are finally removed by filtration.

W. S.

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**Examination of German and other Wines.** By G. GLÄSSNER (Arch. Pharm. [2], cxlix, 117).

THE percentage of alcohol was deduced from the specific gravity of the distillate, and the grape sugar by standard copper solution; the extract was dried at 100°, the author considering that 120°, the temperature employed by many, is apt to cause decomposition.

Name of wine.	Per cent. of alcohol.	Grape sugar.	Free acid.	Extract.	Ash.
65. Hochheimer.....	9·613	0·329	0·461	2·463	0·179
68. Laubenheimer.....	9·994	0·417	0·563	2·736	0·198
68. Markgräfler.....	8·132	0·215	0·515	1·854	0·187
68. Wachenheimer.....	8·200	0·491	0·558	3·801	0·192
68. Bodenheimer.....	10·542	0·333	0·441	1·874	0·186
65. Wachenheimer.....	8·984	0·294	0·529	2·150	0·202
65. Erbacher.....	9·927	0·510	0·515	2·628	0·190
65. Forster Traminer.....	9·569	0·474	0·561	2·444	0·182
65. Rüdesheimer.....	8·989	0·454	0·514	2·916	0·180
68. Dürkheimer.....	7·994	0·263	0·480	2·166	0·171
68. Hambacher.....	7·783	0·255	0·579	2·146	0·178
68. Niersteiner Rehbacher.....	8·981	1·252	0·479	3·120	0·184
68. Zürcher Seewein.....	7·094	0·089	0·650	1·693	0·162
Rother Neuenburger.....	9·630	0·132	0·415	2·440	0·185
65. Casteler v. Schlossberg.....	8·271	0·125	0·550	1·795	0·178
67. Hallauer (Canton Schaffhausen) ..	8·700	0·104	0·381	2·505	0·274
65. Schloss Lenzburger Riesling ....	7·782	0·166	0·600	2·422	0·246
65. Jacobsberger.....	9·414	0·128	0·392	2·138	0·279
67. Yvorne (Waadt).....	9·207	0·167	0·533	1·824	0·195
Tokayer.....	16·836	11·363	0·251	—	—
Xeres.....	20·961	3·571	0·427	—	—
Malaga.....	12·461	—	—	—	—
Petit Medoc Bordeaux.....	10·543	—	—	—	—
St. Julien.....	10·491	—	—	—	—
Cantenac.....	9·782	—	—	—	—
Chateau Larose.....	7·572	—	—	—	—

C. R. A. W.

### Spontaneously Inflammable Loaded Silk. (Dingl. Polyt. J., cciii, 245).

SAMPLES of silk loaded with picrate of lead, were found to ignite by themselves while in the railway waggon. Rubbing such silk between two stones was often sufficient to set it burning.

C. H. G.

### Night-violet. By A. CLAVEL (Dingl. Polyt. J., cciii, 244).

FUCHSINE is digested for twelve hours with iodide of methyl alcohol and caustic soda in an apparatus furnished with an inverted condenser. The mass removed from the apparatus is boiled for a long time with strong soda-lye, which removes all the iodine, leaving the violet as a cake, which is to be dissolved in a mixture of sulphuric acid and water, and then reprecipitated by addition of a little soda. The cake so obtained is washed with a little cold water, dissolved in boiling water, filtered, and the colour precipitated with salt. The violet so prepared appears of its proper colour by artificial light.

C. H. G.



**Preparation of Collodion for Photography.** By VAN MONCKHOVEN (Dingl. Polyt. J., cciii, 323).

It is a fact well known in photography, that after silvering a certain number of plates, the silver-bath suffers an alteration which does not depend on the length of time it is kept, but entirely upon the nature of the collodion and iodized salts employed.

When the collodionised plates are immersed in the silver-bath, a certain amount of organic substance is dissolved out from the collodion. It is found that pyroxylin is partially soluble in water. The water which has been used to precipitate the collodion wool contains a body similar to gelatin in appearance.

To avoid the above-mentioned difficulty, it is recommended that a collodion be employed which is made from precipitated pyroxylin. Forty grams of pyroxylin of good or bad quality, are dissolved in a mixture of 1 litre of alcohol and 1 litre of ether, and the solution is poured into 10 litres of water, well shaken, and the pyroxylin precipitate thrown on a muslin filter. From 20 to 35 grams of collodion wool are thus obtained in light clots of rough texture, not easily ignited, and burning with difficulty. It is perfectly soluble in alcohol, which is a valuable property. A superior collodion may thus be obtained from the worst sample of pyroxylin. As is known, collodion is rendered thick and gelatinous by cadmium iodide, in the iodising process, and fluid by sodium and ammonium iodide; but this is not the case with collodion from precipitated pyroxylin.

W. S.

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**Woodbury's New Photographic Method of Printing.** (Dingl. Polyt. J., cciii, 324).

THIS paper simply describes a modification of Talbot's latest improvement, viz., the gelatin and potassium di-chromate method, and its application of steel plates.

W. S.

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*Dying Cotton with Fuchsine without Mordants* (Dingl. Polyt. J., cciii, 245).

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*Generation of Cold and the Fabrication of Ice by means of Methylic Ether* (Dingl. Polyt. J., cciii, 191—194).

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*Application of Sulphur in the Roasting of Silver Ores in the Stetefeldt Furnace* (Dingl. Polyt. J., cciii, 221—223).

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## PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XVII.—*The Manufacture of Iron and Steel.*

[A Lecture delivered before the Chemical Society, May 2nd, 1872.]

By EDWARD RILEY, F.C.S.

THE title of my paper, "The Manufacture of Iron and Steel," is scarcely a correct one, the subject I purpose bringing before the Society being—a consideration of the elements associated with pig iron; the conditions under which the various elements enter into its composition; the influence they have on the quality of the pig produced; and the part they play in the subsequent conversion of the pig into wrought iron and steel.

The chemistry of the blast furnace has been already so ably brought before the Society by Mr. J. L. Bell, that I do not purpose entering into the consideration of the conditions essential for the economic production of pig iron, further than is necessary to elucidate the composition of the various varieties of it that are made.

The great improvements lately introduced in the manufacture of pig iron, the enormously increased production, at a diminished cost, of what may be considered to be the raw material from which we start in the manufacture of iron and steel are, I think, sufficient to convince not only practical men, but scientific men also, that in any improvement in iron manufacture we must commence with the pig, and consider that our starting point.

One cannot conceive any process so simple and requiring so small an amount of labour as the present system of iron smelting in blast furnaces; we may still further improve that system by diminishing the consumption of fuel, increasing the make, and improving the quality of the pig. Still, with the prospect before us of increased cost for labour, I am at a loss to see how any process can compete with it, except perhaps in very exceptional cases for steel of a high class where quality is the sole object and cost quite a secondary consideration.

Taking pig iron as a starting point, I purpose considering briefly the various varieties of pig iron made from different ores and in different districts.

It is, however, somewhat difficult to give a general idea as to the composition of pig iron in certain districts, as the varieties of ore used are so numerous, and vary so much according to circumstances, that no approximate composition can be given to the pig made.

There are, however, certain districts where, from local circumstances, the same ore and fuel are used constantly. In such districts there is

not much variation in the pig made, each having a distinct character. Such varieties of pig are hematite pig, chiefly made in Lancashire and Cumberland; Cleveland pig, made in the North Riding of Yorkshire, in Durham, and Northumberland; best Yorkshire cold blast pig, Lincolnshire pig, and Northamptonshire pig. In South Wales, Staffordshire, Derbyshire, and Shropshire, so many varieties of ores are used that pig of all descriptions is made. Even in some of the special districts named the large demand for, and the increased cost of native ores (ores of the district), and the advantages derived from the admixture of foreign ores has caused the introduction of the latter, and in some cases necessarily altered the character of the pig produced.

*Clay Ironstones.*

	Low Moor.*	Low Moor.*	Dowlais. Little Blue Vein.
Protoxide of iron . . . . .	36·14	47·13	38·77
Peroxide of iron . . . . .	·61	—	—
Protoxide of manganese . . . .	1·38	2·20	1·30
Alumina . . . . .	·52	—	·32
Lime . . . . .	2·70	2·58	4·45
Magnesia . . . . .	2·05	1·12	4·25
Silica . . . . .	—	—	·08
Carbonic acid . . . . .	26·57	32·55	30·53
Phosphoric acid . . . . .	·34	·96	·46
Sulphuric acid . . . . .	trace	trace	—
Bisulphide of iron . . . . .	·10	—	—
Water { hygroscopic . . . . .	·61	·25	·35
{ combined . . . . .	1·16	1·75	1·08
Organic matter . . . . .	2·40	·30	·29
Ignited insoluble residue . . .	25·27	11·30	17·95
	<hr/> 99·85	<hr/> 100·14	<hr/> 99·83
Ignited insoluble residue . . .	—	—	—
Silica . . . . .	17·37	—	13·47
Alumina . . . . .	6·22	—	2·96
Peroxide of iron . . . . .	·84	—	·40
Lime . . . . .	trace	—	·09
Magnesia . . . . .	·12	—	·15
Potash . . . . .	·65	—	·87
Sulphur . . . . .	—	—	·01
	<hr/> 25·20	<hr/> —	<hr/> 17·95
Metallic iron, per cent. . . . .	29·12	36·70	30·43

\* From Dr. Percy's Metallurgy of Iron and Steel.



In considering the quality of pig iron commercially, taking price as a criterion of quality, it will be found that pig iron which commands the highest price is by no means, chemically speaking, the purest and the most free from the so-called impurities in iron. This holds good, except, perhaps, in one single instance, viz., that of charcoal hematite pig, smelted at Hot Barrow. This pig commands a higher price than any foreign charcoal iron, being used almost exclusively for the manufacture of the best malleable cast iron by annealing castings from the pig in red hematite.

Pig iron made from the clay bands of the coal measures commands the highest price in the market, and it is from these ores that the best qualities of bar iron and boiler plate are made. The high quality of the Low Moor Bowling and generally of the best Yorkshire iron is attributed to the quality of the ore and the freedom of the coal from sulphur.

The coal used is known as the Better Bed coal, and is a thin seam not more than from 16 to 18 inches in thickness. A section of this coal taken through the whole thickness of the bed, and intimately pulverised together, gave:—

*Better Bed Coal Bowling.*

Ash per cent. ....	5·86
Sulphur per cent. ....	·51
Moisture ....	2·21
Coke per cent. ....	68·41
Volatile matter ....	31·59

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100·00

The percentage of sulphur in the coal is certainly low, although I have found coal from other districts as pure, there are few coals in which the sulphur is so low. The coal being coked in open clamps yields a coke with very little sulphur.

The limestone used is the Skipton mountain limestone, and has the following composition:—

	I.	II.	
Silica .....	·28	2·25	
Protoxide of iron .....	·36	·27	
Alumina .....	trace	trace	
Carbonate of lime .....	98·17	93·93	
Carbonate of magnesia ..	1·17	2·12	
Sulphur .....	·03	·21	} sulphide of calcium.
Calcium .....	—	·26	
Moisture .....	·13	·19	
Organic matter .....	traces	·76	
Phosphoric acid .....	traces	nil	
	100·14	99·99	

I have carefully analysed the different numbers of pig iron made at the above works, and find it has the following composition :—

*Bowling Pig Iron.*

	No. 1.	No. 2.	No. 3.	No. 4.
Carbon, as graphite ..	3·421	3·155	3·361	3·308
Carbon, combined ....	·583	·581	·393	·319
Silicium .....	1·708	1·646	1·382	1·381
Iron .....	92·070	92·644	92·952	33·292
Manganese .....	1·606	1·472	1·475	1·169
Phosphorus .....	·630	·635	·602	·602
Sulphur .....	·073	·070	·063	·081
Titanium .....	traces	traces	traces	traces
	<hr/> 100·091	<hr/> 100·203	<hr/> 100·228	<hr/> 100·152

The above numbers were selected by the forge manager, and carefully marked as characteristic specimens ; also two samples, marked 3A and 3B, known as “ mingled metal,” and 3B as “ bull’s eye,” both being No. 3, sample 3B working with a tough cinder short of lime.

	3A.	3B.
Carbon as graphite.....	3·196	3·177
Carbon combined .....	·656	·447
Silicium .....	1·178	1·353
Iron .....	93·370	93·863
Manganese .....	1·241	1·190
Phosphorus .....	·612	·591
Sulphur .....	·071	·060
Titanium .....	traces	traces
	<hr/> 100·324	<hr/> 100·681

On comparing carefully the above analyses, it will be seen that the composition of the pig in the different numbers is practically identical, and the only difference apparent is a slight diminution in the percentage of silicon present. This diminution of the percentage of silicon is much more apparent in hot blast pig, as will be seen in the analyses of the second pig given below :—

*Pig Iron, Seend Wiltshire.*

	Silicium.	Sulphur.	Phosphorus.
No. 1.....	4·717	·036	·867
„ 2.....	3·659	·077	·917
„ 3.....	3·209	·096	·968
„ 4.....	3·140	·196	·724
„ 5.....	2·257	·160	·926
„ 6.....	2·197	·248	·898

The results of the analyses of the Bowling pig would seem to confirm the opinion expressed by Mr. Bell in his paper "On some of the conditions that apparently affect the Quality of Iron," published in the Journal of the Iron and Steel Institute, November, 1871, page 288. He seems to think that the different qualities or numbers of iron are due to the influence of temperature, and that it is an error to suppose that the highly graphitic No. 1 iron contains more carbon than No. 3 or No. 4 iron, or even white pig. I quite agree with Mr. Bell as regards the carbon. In hematite pig it is frequently the case that No. 4 pig contains rather more carbon than No. 1. When the No. 1 pig is siliceous, the tendency of the silicon is to reduce the percentage of carbon.

*Hematite Pig.*

	A. No. 1.	B. No. 1.	C. No. 1.
Carbon, as graphite....	3·548	3·173	—
Carbon, combined ....	·257	1·096	3·756
Silicium.....	3·294	1·660	3·705
Phosphorus .....	·044	·075	·053
Sulphur.....	·065	·071	·046
Iron .....	92·780	93·957	92·361
Manganese .....	·182	trace	·245
Titanium .....	—	·041	traces
	<hr/> 100·170	<hr/> 100·073	<hr/> 100·166
	D. No. 1.	E. No. 4.	White Pig.
Carbon, as graphite....	4·186	3·858	—
Carbon, combined.....	—	—	3·13
Silicium.....	1·817	2·234	·27
Phosphorus .....	·069	·073	·15
Sulphur.....	·035	·115	·54
Iron .....	93·754	93·444	95·83
Manganese .....	·250	·392	·16
	<hr/> 100·111	<hr/> 100·116	<hr/> 100·08

From the above analyses it will be seen that when the silicon is below 2 per cent. the carbon averages rather over 4·2 per cent.; when the silicon is over 3 per cent., the average of the carbon is only 3·8 per cent.

Before, however, accepting Mr. Bell's views, I think we ought to have more correct data to go upon as to the amount of sulphur in pig-iron. In the analyses given of the Seend pig, there is clearly a gradual



increase in the percentage of sulphur with the numbers, except in the case of No. 4, which contains rather more sulphur than No. 5; it disagrees also with the other samples in containing rather less phosphorus, and may possibly have been produced under somewhat different conditions to the other samples.

In Welsh pig-iron I have also found that the percentage of sulphur always increases as the number or the quality of the pig decreases.

*Analysis of South Wales Pig from Clay Ironstones.*

	Grey.	Mottled.	White.	Grey.
Carbon.....	3·14	2·95	2·84	3·08
Silicon .....	2·16	1·96	1·21	2·22
Sulphur .....	·11	·28	·46	·09
Phosphorus ....	·63	·63	·64	·63
Iron .....	94·56	95·39	95·10	94·35
Manganese ....	·50	·23	·14	·33
Nickel and cobalt	·05	·04	·03	·07
	<hr/> 101·15	<hr/> 101·48	<hr/> 100·42	<hr/> 100·77

All cold-blast iron, except column 1, which was made with two tuyeres hot blast and one cold blast.

I am inclined to think that if our methods of determining sulphur were more trustworthy, we should find that slight differences in the amount of sulphur would explain the differences in the numbers or quality of the pig. Sulphur certainly does make grey iron white, and I see no reason why slightly different amounts of it should not modify the pig and produce the differences we find in it.

I am quite ready to admit that the different numbers in grey iron may be produced by difference in the rate of cooling. Take for example the case of the Bowling pig. Practically there is a very great difference in the working of the four pigs marked 3, 3A, 3B, and 4; they were analysed specially to discover this difference, but chemically speaking no difference is apparent. Are we then to assume it is due only to the different temperature at which they are produced?

When No. 3 pig is run from a Bowling furnace large quantities of sulphurous acid are given off, and I must say I am inclined to think that the quantity retained by the pig may differ, and account for the difference in the pig.

With regard to grey cast-iron and white, the conclusions to be drawn from Mr. Bell's paper are as favourable to the view that sulphur causes the white iron, as that it is produced by difference in temperature. On referring to Mr. Bell's paper before alluded to, it will be found that three samples of No. 1 pig gave ·071, ·055, ·063; one of No. 3

pig gave .108; two of No. 4 gave .072, .023, whereas in three samples of white iron .199, .209, and .016 are given. The latter result, .016, is certainly very low indeed for sulphur in a coke made white pig (refer to my analyses), very much lower than I ever found it in such pig.

Mr. Bell in his paper gives the carbon in white iron, so-called uncombined carbon (I presume from this that he considers it combined, or at any rate mostly so), and that the only method we have of determining the difference between combined and uncombined carbon is really of no value whatever. I have long considered that the determination of combined carbon is most unsatisfactory.

Since writing the above I find Mr. Bell has made an experiment with white pig iron from the Clarence Iron Works, and clearly shows that by exposing it to an exceedingly high temperature white pig iron becomes grey—No. 3 and No. 4.

In one experiment 60 lbs. of Clarence white pig was melted in a Siemen's steel melting furnace, and run into a mould of green sand forming a cube 6 in. on a side; with the exception of a trace of white iron at one corner the whole mass was converted into uniform good grey forge.

The same quantity of the same iron was melted on a Saturday and allowed to remain over Sunday in the furnace, during which time it cooled slowly; the block having a maximum diameter of six or seven inches, was entirely grey, chiefly No. 3, interspersed with some No. 4.

It would be interesting to see if by exposure to so high a temperature there was any difference in the percentage of sulphur, and if some may not have been expelled from the white iron.

From the above experiments it is quite clear that by exposing white iron to a higher temperature it is converted into grey iron. Would No. 3 or 4 forge pig be converted into No. 1 pig by exposing it to a very high temperature alone? My impression is that it would not, unless it were heated with carbon, so as to separate the sulphur. I would suggest whether some practical process might not be used to convert hematite No. 4 pig into Bessemer No. 1 by heating at a high temperature with charcoal, No. 4 pig being produced so much cheaper, and without the wear and tear on the furnace that there is in making Bessemer pig.

The method of estimating sulphur in pig iron adopted by Mr. Bell is, I think, open to objection; the method consisted in dissolving the pig in hydrochloric acid, and conducting the evolved gas through potassic plumbate.\*

All so-called pure hydrochloric acid I find contains sulphurous acid,

\* See the Journal of the Iron and Steel Institute for November, 1871, page 277, "On the Behaviour of Phosphorus and Sulphur in the Blast Furnace."

and when large quantities of pig are operated on, large quantities of acid must be used, the results of my experience in employing this method is that even after all the iron is dissolved, and the solution boiled for some time, sulphuretted hydrogen is still given off, seeming to indicate that the sulphur is to some extent in combination with the silicon or carbon; I find this especially the case in siliceous pig irons.

The observation made by Mr. Snelus in his paper "On the condition of Carbon and Silicon in Iron and Steel," published in the Journal of the Iron and Steel Institute, vol. i, for February 1st, 1871, would seem to bear out this view; in this paper he clearly shows that graphite may be separated from grey pig iron mechanically by either sifting out the finer portions of pig borings with a sieve, or washing them away by water. He states, "I was struck with the remarkable and unexpected fact that the finer portions which contained the most graphite contained also an increased percentage of sulphur." In determining sulphur in cast iron, I consider the most accurate method to be to dissolve the pig borings in a flask with 1.50 nitric acid, adding occasionally a few drops of hydrochloric acid; when complete solution has taken place, transfer the liquid to a dish, and evaporate to dryness, adding a few grns. of pure nitre; heat the dish over a small charcoal fire to get rid of all the nitric acid; digest the oxide of iron in strong hydrochloric acid; and evaporate off the excess of acid until there is only just sufficient to keep the oxide of iron in solution; separate the silica and graphite; and precipitate the filtrate with barium chloride in a moderately dilute solution.

The quantity of pig I take is 150 grns.; the 1.50 nitric acid is redistilled before using in a glass retort, and the hydrochloric acid I make myself from salt and sulphuric acid. I have discontinued using gas for heating the oxide of iron, as I have every reason to suppose that the peroxide of iron absorbs sulphur from the gas, and I believe the results obtained in my analyses of the Bowling pig in determining sulphur are not accurate from this cause. (Compare my analyses of Cleveland pig and Mr. Bell's).

*Cleveland Pig, E. Riley.*

	I.	II.
Carbon, as graphite .....	2.97	2.881
Carbon, combined .....	.51	.352
Silicium .....	1.48	1.491
Phosphorus .....	1.82	1.739
Sulphur .....	.20	.223
Iron .....	91.92	92.445
Manganese .....	.66	.344
Titanium and vanadium....	.24	.252
	<hr/> 99.80	<hr/> 99.727



I. Mean average composition of Cleveland forge pig 3 and 4, the drillings from six different pigs taken promiscuously from the iron being used at Hawke's Crawshay's works at Newcastle.

II. No. 4 Cleveland pig from the Newport Iron Works, B. Samuelson and Co.

For determining sulphur in steel and wrought iron, I believe absorbing the sulphuretted hydrogen in a salt of lead or silver to be accurate, if sulphuric acid is employed instead of hydrochloric.

Another argument in favour of the view I take is that you may have No. 3 or No. 4 pig containing  $\frac{2}{10}$  to  $\frac{4}{10}$  per cent. of sulphur, whereas I never examined a No. 1 pig that contained more than .07 per cent. of sulphur; usually it contains less.

Surely, then, if the difference between No. 1 and No. 3 or 4 pig was only due to being produced at a different temperature, or to difference in cooling, we ought to find occasionally  $\frac{2}{10}$  per cent. of sulphur in the No. 1 pig, unless we assume that the graphite in crystallising out separates some sulphur from the pig.

It certainly would be an interesting experiment to cool slowly some No. 4 pig containing say  $\frac{2}{10}$  to  $\frac{3}{10}$  per cent. of sulphur under blast-furnace cinder, and examine the No. 1 iron produced, and see if the amount of sulphur present were less; my impression is it would be found to be so.

It is generally admitted that the best pig iron is made from the clay ironstones of the coal measures, whether it is used as pig or for the purpose of making wrought iron; this applies equally to hot and cold blast, the latter differing from the former in containing rather less silicon. I think it a fair inference to make, that pig iron having the composition of Low Moor, or Bowling, or say Blaenavon or Pontypool pig, or pig made with the same ores, and equally good fuel, is, under our present system of manufacturing wrought iron, a type of what is best adapted for making the best qualities of plates and bars.

At works where the best iron is made, and the pigs are all purchased, I have found, on analysing the different pigs used, that the mean average composition very closely assimilates that of pig made from the clay band ironstone.

The pigs used were—

	Silicium.	Sulphur.	Phosphorus.
No. 1. Swedish.....	.658	trace	nil
„ 2. Wosborough Dale ..	1.114	.346	1.023
„ 3. Baber's Field .....	2.634	trace	.478
„ 4. Morley Park .....	1.504	.085	.631
„ 5. Beeston Manor ....	.942	.089	.272
„ 6. Ditto, with red ore ..	1.250	.156	.337
Mean.....	1.350	.062	.456

Whereas in irons that are chemically very pure, such as the Swedish in the above table, or carburised melted wrought iron made by Parry's process, which is nearly free from silicon and phosphorus, the wrought iron produced is very red, short, and quite unfitted for the manufacture of wrought iron of the best quality, unless mixed with other iron containing some silicon and phosphorus.

From this I am led to conclude that silicon and phosphorus do play an important part in the manufacture of iron, and that when they are present within certain limits they are beneficial and serve a purpose.

I quite agree with Dr. Percy that the superior quality of the best Yorkshire iron is due to a great extent to the skill and care used in its manufacture, and I think that equally good iron may be made from the best Staffordshire or South Wales ores with their best coal if the same process of manufacture were employed.

Having considered the composition of pig made from clay ironstone, I purpose considering briefly that of pig made in other districts; the most important of these is perhaps Cleveland. Mr. Bell has published an elaborate series of analyses of this pig in his paper before alluded to.

The peculiarity of the Cleveland ore is the rather high percentage of phosphorus it contains and the excess of alumina, the alumina being present in a larger proportion than half the percentage of silica, it being generally admitted that the proportion of silica to alumina should be 2 to 1. On this account the pig made is rarely very siliceous, and from the composition of the ore I attribute the advantage of using blast of a very high temperature, whereas blast heated to an excessively high temperature with siliceous ores would in all probability largely increase the percentage of silicon in the pig.

In the analyses given by Mr. Bell he includes in the composition of the pig a certain amount of slag, varying from '36 per cent. to 2'02. I cannot say that in all my experience I ever found any evidences of slag in pig iron when it was perfectly solid and the pig carefully bored after removing all the outer skin.

On dissolving pig iron in dilute hydrochloric acid to separate the graphite, filtering off the residue, dissolving the silica in dilute caustic potash and burning off the graphite in a muffle, I have found in various pig irons the following residue:—When the pig contains much phosphorus, such as Cleveland pig, it is necessary to use much stronger hydrochloric acid and to boil the solution well and for some time, or the residue, after burning the graphite, will consist of phosphate of iron from the phosphide of iron, which is only soluble completely in strong hydrochloric acid.

Thus when the same sample of Cleveland pig was treated with dilute

acid, 255.57 grms. left a residue on burning the graphite of 4.12 grns., whereas on treating the same pig with stronger acid and boiling, 177.48 grms. left a residue on burning the graphite of .71, consisting almost entirely of titanitic acid with a little oxide of vanadium. With hematite pig dilute acid will dissolve out all the iron, and on heating the silica as above described and burning off the graphite, only a very small residue is left—

	Grms.	Graphite.	Residue on burning.	
Bessemer pig, No. 1 ..	254.07	10.18	.475	{ Titanic acid = .108 per cent. Ti.
„ 1 ..	248.6	8.06	.170	{ Titanic acid = .041 per cent. Ti.
„ 1 ..	238.66	9.30	.945	{ Titanic acid, with a little iron, = .24 per cent. Ti.
„ 1 ..	244.62	8.81	.135	{ Chiefly iron, with a little PO <sub>5</sub> .
Staffordshire pig } Shelton .... }	4 .. 273.98	8.53	.73	{ After fusion with pot. bisul. gave TiO <sub>2</sub> , .53 = Ti per cent. .117.
Hematite, No. 4 ....	286.3	8.63	.21	Trace of TiO <sub>2</sub> .
„ 4 ....	256.43	6.99	.20	Ti, per cent. .04.
Cleveland pig 3 and 4, mixture of six samples .....	169.18	8.51	.24	{ Ti, per cent. .08, contained a little iron.
Gartsherrie .....	242.15	6.75	.77	{ Oxide of iron and PO <sub>5</sub> , and some sand sent with pig borings.

I find that a little phosphate of iron almost always remains with the silica from pig iron, and in accurate analyses the silica should be driven off by hydrofluoric acid, and the remaining phosphate of iron added to the phosphorus determination. I invariably find titanitic acid in the residue from the graphite in hematite pig; frequently the residue is pure titanitic acid.

Hematite pig requiring only dilute hydrochloric acid to dissolve it; if any slag existed in the pig, surely it ought to be left with the graphite.

In dissolving pig iron in neutral chloride of copper and using a little dilute hydrochloric acid to dissolve any basic iron salt, I have never been able to get any indications of the presence of slag in pig iron, or have never been able to find satisfactorily aluminium in pig iron; if the pig contained slag it certainly ought to be present.

I have entered somewhat fully into the question of the presence of slag in well run and solid cast iron, as I think the point ought to be definitely settled.

Hematite pig is special in its character on account of its freedom



from phosphorus and its adaptability for the Bessemer process. All the hematites are more or less siliceous, the Cumberland ores being less so than the Lancashire ores. Hematite pig is decidedly siliceous, and the efforts of manufacturers of this pig are always directed to reduce the amount of silicon present. The introduction of aluminous ores in the furnaces from Belfast and Antrim materially modifies the percentage of silicon and reduces it in some cases in the pig to below 1 per cent. Hematite pig, however, rarely contains less than 2 per cent. of silicon, and it not unfrequently contains 4 or 5, and even more. Amongst several samples recently examined I have found—

	No. 1.	Light-coloured grey glazed pig.	No. 1.	No. 1.
Silicum ....	4.287	5.652	3.756	3.963
Sulphur ....	.041	.103	.046	.037
Phosphorus..	.057	.055	.033	.036

No. 1 Bessemer pig may contain over 4 per cent. of silicon without there being any apparent difference in its fracture, although with this percentage of silicon the strength of the pig will be materially reduced.

In the manufacture of Bessemer pig from siliceous hematites there are all the conditions essential for making siliceous pig, viz., an excess of fuel and an exceedingly high temperature.

The percentage of phosphorus in hematite pig rarely exceeds  $\frac{1}{10}$  per cent., and is frequently not more than .03 to .05.

Scotch pig made from black band is very similar in its composition to the best Cleveland; it contains, however, less phosphorus; the average would be about 1 per cent. or perhaps rather over. It is considered to be a stronger and rather better pig than Cleveland.

Northamptonshire pig smelted from the Northamptonshire oolitic iron ores is a weak pig. The percentage of phosphorus in it is high, about the same as that of Cleveland and the silicon also high, especially if it is smelted with hot blast.

Lincolnshire pig from the Lincolnshire oolitic ores, which contain mostly an excess of lime, is much less siliceous in its character than the Northamptonshire pig, the phosphorus is also lower.

Having considered briefly some of the general characteristics of the various descriptions of pig iron, I purpose next considering the elements which enter into the composition of pig iron.

The chief constituents of pig iron are carbon silicon, sulphur, phosphorus and manganese; besides these, there are usually present traces of copper and titanium (the latter in grey iron only), frequently nickel and cobalt, and occasionally vanadium and arsenic.

The percentage of carbon in the best varieties of pig iron varies from

3 to rather over 4 per cent., except perhaps in the variety of iron known as *Spiegeleisen*, which sometimes contains nearly 5 per cent.; I have, however, never found it as high 5, although some authors give as much as 6 per cent.

Silicon when present in large amount, as in *Bessemer pig*, reduces the percentage of carbon, as before mentioned; in inferior pig iron, containing much sulphur and phosphorus, the carbon is always low.

	Staffordshire.		Locality not known.	
	I.		II.	
Carbon .....	1·337		1·982	
Silicium .....	·462	·488	·912	
Sulphur .....	1·130	1·121	·567	
Phosphorus .....	3·967	3·874	2·910	
Manganese .....	·221		1·055	
Iron .....	93·011		93·615	
	<hr/>		<hr/>	
	100·128		101·041	

I cannot at all agree with Mr. Bell that a reduction in temperature in the furnace is chiefly the cause of the production of white iron. I believe it to be due to sulphur. If a furnace is worked with a very sulphury coke the iron will be white, although you may have a sufficient burden of fuel in the furnace to make the iron grey if the coke were not sulphury. Coke or coal-made white iron in my experience always contains more sulphur than grey iron, and I believe it impossible to reduce the percentage of sulphur below  $\frac{1}{10}$  per cent. even with the very best north country coke; white iron in my experience does contain rather less carbon than grey pig made from the same materials.

Take the analysis of two samples of Staffordshire pig, in which the sulphur was in one case ·61, in the other ·36, and also in the analysis previously given:—

	White pig with few specks of mottled in centre.	Good mottled pig.
Carbon .....	2·30	2·59
Silicium .....	1·36	1·11
Phosphorus .....	1·02	1·06
Sulphur .....	·61	·36
Iron .....	94·93	94·36
Manganese .....	·81	1·43
	<hr/>	
	101·03	100·91

When the sulphur in one pig is about double that in another, the carbon is reduced more than  $\frac{6}{10}$  per cent.

The most satisfactory way of determining whether the amount of carbon is due wholly to the temperature at which the iron is produced, or the rate of cooling, would be to examine the pig, white and grey, made from charcoal where there is practically no sulphur in the iron. As the furnace works quicker when making white iron, I am inclined to think that white iron does contain less carbon than grey iron, as the iron has not had time by being sufficiently long in contact with the fuel to take up the full amount of carbon.

Sulphur in pig I believe to be entirely derived from sulphide of iron in the fuel, originally from pyrites, or from any sulphide of iron that there may be in the ore. The best cokes all contain a mixture of metallic iron and sulphide of iron; in some, after burning off all the carbon, there still remains sulphide of iron in the ash. I differ from Mr. Bell in his supposing that the iron takes sulphur from the calcium when silica and alumina are present in such quantity as only to produce a vitreous slag; good grey iron, No. 3 and No. 4, Bowling, for instance, is made with a vitreous cinder. I think it more probable that the excess of lime acts upon the sulphide of iron in the coke and ore, and converts it into sulphide of calcium and metallic iron. By using a heavy burden of lime in a blast furnace, grey iron may be made even when some quantity of finery, flue, or forge cinder is used; it is well known that such materials contain some amount of sulphide of iron; the sulphur must necessarily be taken out by the calcium of the lime. If simply a lower temperature were the cause of iron being richer in sulphur, then, clearly, of two furnaces working, one with hot blast and the other with cold, and both making white iron, the cold-blast iron ought to contain more sulphur than the hot blast; few, however, will accept this view as correct. Mr. Bell maintains that the temperature of a hot-blast furnace is not higher than that of a cold-blast furnace, as the hot-blast furnace has to smelt more materials than the cold blast. This conclusion I think open to question.

I have known coke that has been condemned as too bad to be used at an ironworks, to have been used after exposure to the weather for two or three years when fuel was short, and good iron to have been made from it; this I attribute to the gradual oxidation of the sulphide of iron in the coke, and to its being washed out by the weather.

I know also some descriptions of coke that give on analysis a very high percentage of sulphur, and still they make a fair quality of iron on account of much of the sulphur existing as sulphide of calcium.

In making Bessemer pig, is not the heavy burden of lime and fuel used to make No. 1 iron, to insure that the pig contains a minimum amount of sulphur? or if it were not so, why should not No. 3 answer as well for the Bessemer process; the silicon is decidedly lower, and



it contains often as much carbon as a highly siliceous No. 1 pig? It will be seen, however, on referring to my analyses, that there is a distinct difference in the percentage of sulphur.

All blast-furnace cinder is, in my opinion, sufficiently basic to retain the small amount of sulphur it contains, and the percentage of silica would have to be largely increased before it would drive off any sulphur from the calcium.

The question as to whether carbon forms any definite compound with iron is, I think, open to great doubt. Iron seems to have the power of dissolving carbon at a high temperature, and on slow cooling the carbon is separated in distinct graphitic scales. If the cooling is very slow, large crystals  $\frac{1}{2}$  to  $\frac{3}{4}$  of an inch long are formed, and graphite may readily be removed from the faces with a knife. On chilling grey iron, the carbon is retained in a more intimate state of combination or solution, and cannot be separated. As to whether the carbon is chemically combined or whether it is carbon in another form than graphite simply dissolved in the iron, different opinions exist.

Mr. Snelus, in his paper before alluded to, has clearly shown that the graphite may be separated from grey pig mechanically, either by sifting out the finer portions from pig borings, or floating off the lighter portions by water, and collecting them. By these methods he has found as much as 9.11 and 28.48 per cent. of carbon in the finer parts of Bessemer pig, and 7.015 and 41.392 in the fine portions of Middlesborough pig.

*Silicon.*—Silicon is an element that is always present in every form of iron, although at times its quantity is very minute, and in wrought iron it is possible the silicon may be due to the cinder between the layers or fibres of the iron.

With regard to silicon, I think we have much to learn as to the different conditions in which it exists in pig iron and steel. We know that carbon exists in three different forms, and that silicon has also the amorphous, the graphitic, and crystalline forms of carbon. It appears to me to be a fair inference that silicon does exist in, at any rate, two different forms in pig iron and steel, and that we may eventually be able to explain many points in the manufacture of iron and steel when we are able to determine the different conditions in which the silicon exists.

I have stated that in the manufacture of Bessemer pig, all the conditions exist for making a highly siliceous pig when siliceous iron ores are used; except perhaps if the object were to alloy silicon with the iron, less flux would be added. Such pigs, the analyses of which I have given, can only be used for the Bessemer process with great loss of yield, as all the silicon has to be oxidised and converted into silicate of iron, assuming the formula of the cinder to be  $3\text{FeO}.\text{SiO}_2$ . Then every

per cent. of silicon will require about 4 per cent. of iron to flux it away. Bessemer-converted cinder possibly contains more silica than any cinder.

As to the conditions in which silicon exists in cast-iron, there are different opinions, Mr. Snelus, in his paper on carbon and silicon in iron and steel before alluded to, is of opinion that it all exists in combination with the iron; Mr. Bell differs from this view, and quotes some instances where silica separates from pig iron.

I quite agree with Mr. Bell, as I have frequently found that silica does separate from cast-iron. On the bearings of rolls I have found a thin skin that readily peels off, consisting of a mixture of perfectly white silica intermixed with small crystals of cast-iron. This usually occurs in faulty rolls; the rolls are cast on end, one bearing up, the other down; on the upper bearing near the dead head, I have found this skin peel off.

I have also found, on examining hematite pigs, that the silicon often separates in very different forms under the same conditions, sometimes very bulky, at other times very dense, so that I have frequently thought there was a small percentage in pig iron when it has been very high on account of the dense form of the silica.

Some of the silica is readily dissolved in dilute acid whilst a portion remains in a hard gritty form undissolved. It was my intention to have carried out a series of experiments on some of the pigs of which I have given the analyses; I regret to say, that on account of a recent illness, I have been unable to do so.

Siliceous pig is frequently made accidentally at ironworks, and is known as glazed or blazed pig. When a furnace is newly blown in, this occurs; it is probably due to the excess of fuel that is used in blowing in a furnace.

When any poor materials are used in a blast furnace, a siliceous pig is the result; thus some very poor black-band ironstone, smelted at Dowlais, containing only about 10 per cent. of iron, made a siliceous pig containing  $7\frac{1}{4}$  per cent. of silicon; a sample of Scotch pig has been found to contain as much as 8 per cent. of silicon. I have also known the small rubbish from mine kilns, when it has accumulated and been used in a blast furnace, to make siliceous pig.

There is an impression amongst chemists that silica, when it exists as soluble silica, has a tendency to make siliceous iron. One would suppose, arguing wholly on chemical grounds, that finery or forge cinder would make such iron; practically, however, it is just the reverse; pig iron smelted wholly from cinders, and known as *kentledge*, contains only from two to three-tenths per cent. of silicon; the only conditions under which cinders make siliceous iron are, when they have been roasted and made infusible.

I have recently made some experiments to determine the largest amount of silicon I can alloy with iron by heating oxide of iron, clean quartz sand, and an excess of carbon together. The following mixture was used; the red ore was soft red hematite, containing 65·4 per cent. of metallic iron:—

Red ore .....	6 $\frac{1}{2}$ lbs.
Sand .....	6 $\frac{1}{2}$ „
Wood charcoal .....	2 „ 13 $\frac{1}{2}$ ozs.

The above mixture was heated in a Siemen's furnace, melting tyre-steel for 48 hours in a black-lead steel pot. On the top was sprinkled a layer of charcoal. The mass had fallen to about one-third of the height of the pot, the powdered charcoal remaining on the top. On breaking the pot, a large, irregular-shaped fused mass was found at the bottom, weighing 3 lbs. 7 ozs. The sand still retained its granular form, although it was semi-fused, with occasional patches of fused vitreous cinder with a purplish tinge, and quite transparent.

Buttons of iron were interspersed through the mass, in some places in the midst of charcoal, in others, finely imbedded in the semi-fused sand without charcoal. Some of the buttons were silvery-white, graphitic on the exterior, and very brittle; others imbedded in the sand without charcoal were quite malleable, flattening considerably before breaking on the exterior. These buttons had a yellowish and some a reddish tinge, the fracture was decidedly steely and fine in the grain.

The large lump of siliceous iron contained 17·96 per cent. of silicon.

The brittle small buttons ..... 21·71 „ „

The malleable buttons ..... 3·72 „ „

The alloy is quite insoluble in hydrochloric acid, and only slightly soluble in aqua regia, after boiling for some time. The silicon was determined by fusing the finely pulverised alloy in a gold crucible with a mixture of carbonate of soda and nitre.

An experiment was also made with cinder prepared by heating some of the same ore with sufficient charcoal and sand to make a fluid silicate of iron. After fusing the silicate it was run out, intimately pulverised, and simply mixed with an excess of charcoal and put into a steel pot in the same Siemen's furnace for 48 hours. On taking out the pot, a large button of irregular shape was found at the bottom, weighing rather over 4 lbs. The silica from the silicate was perfectly fused, and was quite free from iron, with a darkish shade, and similar in appearance to obsidian. The alloy on analysis was found to contain 18 per cent. of silicon.

From the nature of the experiment, from the intense heat the materials were submitted to, and the excess of carbon and silica pre-



sent, one may fairly assume that 22 per cent. is the maximum amount of silicon that can be alloyed with iron by simply heating silica, charcoal, and oxide of iron together.

A silicide of iron of the formula  $3\text{FeSi}$  would require 20 per cent. of silicon; the alloy will probable contain some 2 per cent. of carbon, so that I think it a fair assumption to consider the bulk of the alloy to represent silica in which the oxygen is replaced by iron.

The highest percentage of silicon found in any product from an iron works was found by Dr. Percy in an old bear (hearth of a blast furnace after blowing out) from Tow Law; this iron contained 15.3 per cent. of silicon.

There appears to me to be no difficulty in making siliceous iron in a blast-furnace containing 10 to 12 or even a higher percentage of silicon. Possibly the fact of its being unattacked by acids may make such an alloy available for some purposes, as it will keep bright when exposed to an atmosphere impregnated with acid fumes. The alloy is exceedingly brittle, and may be easily broken by a tap with a hammer.

Quartz, when it exists as such in the ore, more especially the dense hematites of Lancashire, Cornwall, and Devonshire, always makes a much more siliceous pig than porous light ores, even though the latter contain some amount of amorphous silica; this may be accounted for by the fact that light porous ores are much more readily smelted than dense compact ores—compact ores such as magnetic oxide of iron and micaceous ores, similar to that from Elba, are not easily smelted on account of their dense and close structure. Such ores, in fact, I may say all ores, are improved by being calcined; it seems to open the pores of the ore, to make it more readily permeable by the gases of the furnace, and more easily fused. In roasting ores, however, care should be taken not to fuse them, or even partially fuse them, as I consider many ores when fused are really of no more value than finery forge or flue cinder.

*Phosphorus*.—Practically speaking, all the phosphorus in the ore and in the fuel used, passes into the pig iron made. The series of analyses I made of blast-furnace cinder from all the furnaces, 17 in number, at Dowlais some years since, clearly proved this. When the cinder was grey all the phosphorus passed into the iron; it was only when the furnace was running on a scouring cinder or cinder containing iron, that the phosphorus passed into the slag (see Percy's *Metallurgy*, page 499).

When furnaces work with the same materials, and the cinder is grey, I have found that the percentage of phosphorus is practically a constant quantity. This will be seen on referring to the analyses of the South Wales pig, Bowling pig, and Seend pig. I should have thought this would have held good with the Cleveland pig, although the analyses of Mr. Bell do not seem to show that it is so. Phosphorus, like silicon, unquestionably makes pig iron weak, although

I am inclined to think that when the amount is not more than  $\frac{1}{2}$  to  $\frac{3}{4}$  per cent., the strength of pig iron is not affected by it. I have found occasionally best Yorkshire cold-blast pig to contain as much as nearly  $1\frac{3}{4}$  per cent. of phosphorus. It contained—

Silicon, per cent. ....	·94
Phosphorus.....	1·67

This pig was very tender, although when used in making best Yorkshire iron, it did not materially affect the quality of the bars. Its production was due to the use of a thin seam of clay-band ironstone containing 3·27 per cent. of phosphoric acid.

*Manganese.*—All grey manganiferous pig that has been made in this country I have found to be very siliceous; this is due chiefly to the ores used containing much quartz. The pig made from the spathose ores at Tow Law is of this character; it is a hard iron, and chills easily; it is used largely for making plough-shares; they are cast in a mould, one side of which is formed by cast iron, the other by sand. Although the thickness of the casting is not more than  $\frac{1}{4}$  to  $\frac{3}{8}$  inch thick, it is on one side quite white to the centre, on the other perfectly grey, the grey iron giving strength to the brittle, chilled, and hard-cutting exterior of the share.

The effect of manganese in making a peculiar pig called Spiegeleisen, is well known. Formerly this pig was all made on the Continent; it is now being largely manufactured by the Ebbw Vale Iron Company, from the spathose ore of the Brenden Hills. I shall consider the effect of manganese on iron when treating of steel.

With regard to other elements that are occasionally found in pig iron, I find traces of copper and a little titanium in all grey pigs. Cobalt and nickel I find in pig made from the clay ironstones of the coal measures, and in Cleveland pig, also titanium and vanadium in the latter. Vanadium I find in the oolitic ores from Wiltshire in very appreciable quantity (see my paper on “Vanadium in Pig-Iron,” *Quarterly Journal of Chemical Society* for 1864). I have also found it in Lincolnshire pig, and my impression is that it will exist in most pig made from oolitic ores; arsenic exists in some hematite pig.\*

The above elements I believe to be merely accidental impurities reduced from the iron ore, and that they have no bearing whatever on its quality, unless they are present in unusual quantity.

Much virtue has been ascribed to titanium, more especially by Mr. Mushet, who has numerous patents for its use and application. I must say, however, that after an experience of 12 years, I have failed to be convinced that there is any virtue in it whatever.

\* Since writing the above, I have found it in three samples of pig smelted from Northampton ore.

Titanium does enter into the composition of most grey pig irons, or, I should say, may be found in most of them. In white pig iron, in wrought iron, and steel, I have always failed to detect it, even when titanic ores have been used wholly for making the pig. If titanium is alloyed with iron, it ought to be found in steel and white iron. My impression is that it exists disseminated through the pig in some form similar to the nitrocyanide, although I have never been able to detect the red crystals in the silica or graphite from pig containing titanium.

In some cases when titaniferous ores are used to the extent of about 5 per cent. with hematite ores, the pig made appears to be stronger; the evidence, however, on this point is open to question.

The use of ores containing titanium in the blast furnace has the effect of giving a blacker and darker colour to the iron made.

Hematite pig is undoubtedly improved by using an admixture of aluminous ores, such as the Antrim or Belfast ores, which contain titanic acid. The effect of the titanium is to give the pig a darker colour, and commercially this is advantageous, although I think the benefit of the use of these ores is due to the excess of alumina the ores contain.

Titanic ores have been smelted at Norton, for the last four or five years, and unquestionably a very good pig iron is made, more like refined metal in its character than white pig. This is due to the very small percentage of silicon present in the iron; the ore used is quite free from quartz, or any free silica, the gangue being labradorite.

The percentage of iron in the Norwegian titanic ore\* is so low, and that of titanic acid so high, that the amount of flux and fuel required to smelt it is very large. Practically, smelting titanic ores in this country is a failure; this I clearly pointed out before the attempt was made. The ore contains from 40 to 45 per cent. of titanic acid, and yields in bulk less than 30 per cent. of metallic iron. The best flux is dried clay or old bricks and limestone, so as to form a cinder to flux away the large excess of titanic acid. The furnace cannot be worked with a heavy burden of lime, as the titanic acid then forms a difficultly fusible cylinder; consequently the iron is usually white, and mottled or grey iron is produced with difficulty.

I never was able to see how it could pay to bring an expensive material from Norway, containing more than  $\frac{2}{5}$ ths of its weight of a difficultly fusible mineral acid, and consequently a low percentage of iron, the titanic acid requiring a large amount of flux to run it away in the cinder, and necessarily a large quantity of fuel to melt it, when charcoal pig could be brought in this country at fully less than 20s. per ton than the titanic pig costs in making.

The virtues of titanium, although extolled by Mr. Mushet and others,

\* The above remarks refer to ilmenite.



and for a time thought favourably of by myself, are more than questionable. I believe there is no virtue whatever in titanium; ilmenite may be useful for certain purposes, as a highly refractory material for lining furnaces, but even for this purpose its use will be limited, on account of the effect it has of making iron cold-short.

In considering the quality of iron made from various ores, I have spoken generally, assuming that fuel of a fair quality was used. The quality of fuel is of even more importance than that of the ironstone, as even inferior ores when smelted with charcoal, make a good quality of pig iron. In the south of France I have seen spathose ore used which contains a large percentage of pyrites. The ore is roasted with small charcoal, and then spread out and exposed to the air before using. The furnaces are worked rather heavy on limestone, and the sulphur is all separated; this, I think, clearly tends to uphold my view, that the lime acts on the sulphide of iron.

Fortunately for this country our supply of coal is large, and much of it is of excellent quality. Many of the South Wales coals and the Staffordshire coals contain not more sulphur than  $\frac{3}{4}$  to  $1\frac{1}{4}$  per cent. Coals containing this amount, when used in the blast furnace, make an excellent quality of iron. The largest and most important district, viz., Northumberland and Durham, produces the most compact and densest coke in the kingdom, and supplies iron works with it at a distance of 150 miles.

From a very extensive experience in the examination of north country cokes, I may state that the best cokes contain from  $\frac{7}{10}$  to  $\frac{9}{10}$  per cent. of sulphur, and from 5 to 8 per cent. of ash; cokes containing from  $\frac{9}{10}$  to  $1\frac{2}{10}$  per cent. would be considered of very fair quality; above this the coke may be considered inferior. I have found as much as 3 per cent. in some north country coke. This coke was exceedingly hard and dense, some of the hardest I ever examined. In cokes from other districts I have found as much as  $4\frac{3}{4}$ ; the coke was hard and bright, and as far as could be judged from appearance, a good coke.

Coke containing say from  $\frac{7}{10}$  to 1 per cent. of sulphur is adapted for making the best descriptions of iron, and for Bessemer pig it may even be used up to  $1\frac{1}{4}$  per cent. When the percentage amounts to  $1\frac{3}{4}$  per cent., it is difficult to make No. 1 pig, unless a very heavy burden of limestone is used; with 2 per cent. of sulphur great difficulty would be experienced in making No. 1 pig; and with coke containing 3 per cent. of sulphur, it would be difficult to produce anything but white iron.

In considering the value of coke, not only the percentage of sulphur should be considered, but the state in which the sulphur exists. The most prejudicial form is when it occurs as sulphide of iron; when the sulphur exists as sulphide of calcium, I believe it has no prejudicial

effect on the iron. Large quantities of sulphur may be present in a blast furnace, as a sulphate of an alkaline earth, without having any effect on the quality of the iron produced. I have seen an iron ore smelted containing a very large percentage of sulphate of baryta. The ore in bulk would contain 15 to 20 per cent. of sulphate of baryta; this was reduced to sulphide of barium, which floated on the pigs in the form of a matt containing some sulphide of iron; the iron below was grey, and of good quality.

### *Refined Iron.*

Having given a hasty description of the various varieties of pig, I purpose passing on to the conversion of the pig into wrought iron.

The process of refining iron in the old finery is still carried on at some works; it is, however, mostly superseded by what is known as pig-boiling, that is, puddling the pig directly instead of refined metal.

In refining iron it has been clearly shown by Price and Nicholson and others that the silicon is oxidised before the carbon, and in some cases silicon is separated completely from the metal, existing only as traces.

The time required to refine iron seems to depend on the amount of silicon present in the pig; thus, grey iron requires much longer than white, and when very siliceous white iron or glazed grey pig is used, it is almost impossible to refine it. I have known white pig containing over 2 per cent. of silicon blown for seven hours, and then it was not metal. The finery cinder produced differs very much in appearance; it contains 5 or 6 per cent. more silica than ordinary finery cinder from pig with a moderate amount of silicium in it.

With common iron, such as white Welsh or Staffordshire pig, the effect of overblowing is to convert the iron into a spongy porous mass, similar to what is known as a skull, whereas with best Yorkshire iron I have seen wrought iron on the top of the metal, the metal being quite solid. I cannot, however, say that the latter metal was overblown; it may probably be due to the production of wrought iron near one of the tuyeres.

In refining, the larger portion of the silicon is separated, and some amount of sulphur and phosphorus with a little carbon. In considering the question as to the best composition of pig iron for refining, and the same will apply to puddling, I am decidedly of opinion that when pig contains much sulphur and phosphorus and as a rule the percentage of carbon is low, it is advantageous to have a certain amount of silicon present, so that the silicon may be acted on before the carbon and give time for more of the sulphur and phosphorus to separate, whereas if there is but little silicon the carbon is attacked, the metal is soon sufficiently blown before you have separated any amount of sulphur

and phosphorus. Time is an essential condition in their separation, and, with regard to the phosphorus, it is gradually oxidised by the oxides of iron present in the cinder, and converted into phosphate; possibly some may separate as phosphide of iron; the sulphur, most probably, is all separated as sulphide of iron.

Take such common pig iron, the analysis of which I give on page 554. This contains only .46 per cent. of silicon; or take cinder iron, which will contain about .25 per cent. of silicon. Such iron is blown in a very short time, and very frequently converted into honey-comb metal, whereas if the pig contained from 1 to  $1\frac{1}{4}$  per cent. of silicon it would be much better refined.

The best common iron contains from 1 to  $1\frac{1}{4}$  per cent. of silicon. Such iron has a smoother face than inferior pig, and when struck with a hammer, rings, is brittle, and crystalline; whereas inferior pig, containing only 2 to 4 tenths of silicon, is rough on the face or surface, and is covered with pea-like lumps, breaks with less ease than the crystalline pig, and when struck strikes dead like lead, without ringing at all. Such pig when puddled can be scraped together by the puddler very rapidly, coming to nature very soon, but at the same time producing a very inferior puddle bar.

Samples of white pig, of which the analysis was given, page 545, or the two following analyses, may be taken as a fair sample of the composition of Staffordshire and Welsh common pig. The analyses given were made to see if there was any chemical difference in the composition of the iron when cast in sand or in cast iron chills. There appears to be no very marked difference in the composition, as one would have anticipated.

*Good Welsh Common White Forge Pig.*

	I.		II.	
Carbon . . . . .	2.25	2.26	2.37	2.48
Silicium . . . . .	1.14		1.09	
Phosphorus . . . .	.82		.76	
Silicium . . . . .	.77		.73	
Manganese . . . .	.17		.22	
Iron . . . . .	95.87		95.58	
	<hr/>		<hr/>	
	101.02		100.75	

*Puddling.*

The process of puddling consists in melting the pig in a reverberatory furnace and exposing the molten iron to the action of a current of air, the iron in the meantime being vigorously stirred so as to expose fresh surfaces of iron to the action of the air, and to mix the melted iron



more thoroughly with the oxides of iron in the form of hammer-slack and cinder that are always used.

The oxygen of the air is introduced by the rabble-hole in the door. The process of puddling is however materially assisted, and the quality of the iron improved, according to the nature of the material (fettling) used for lining the sides of the furnaces, known technically as the boshes. It is necessary to use some material at the sides round the furnace to prevent the wash of the iron rapidly destroying them.

The best materials for fettling are unquestionably the purer oxides of iron, such as pure hematite, roasted spathose ore, magnetic oxide of iron, Bilboa ore, pottery mine (roasted carbonate of iron very free from earthy matter).

In selecting a material for fettling, it is necessary that it should be as free as possible from quartz or sand; a certain amount of clay is not injurious, although it will necessarily tend to make the fettling melt away sooner and not last so long.

The hard siliceous hematites are not adapted for fettling. Thus in two samples of fettling ore examined—

	I.	II.
Siliceous matter per cent. . .	30·36	6·64
Peroxide of iron . . . . .	65·87	90·15
Moisture . . . . .	1·11	1·09

the siliceous matter in I was chiefly clay, whereas in II it was mostly quartz. Sample I proved to be a much better fettling than sample II.

The best fettling material is what is known technically as best tap; this is the cinder from a heating furnace where piles of wrought iron are heated before being rolled, the bottom being made of cast iron and known as a cinder bottom, in distinction from the ordinary brick bottom covered with sand.

A furnace fettled wholly with best tap has such an effect on the quality of the iron, that even from very inferior pig or cinder pig good iron may be made, and from pig of fair quality more puddle-bar can be got out than the weight of pig iron put in.

In the process of puddling, the quality of the iron is, however, in a great measure dependent on the workman, both as regards the yield and the quality of the iron produced.

Since the invention of puddling, one of the greatest improvements in the manufacture of iron was the introduction of cast iron bottoms in puddling furnaces, instead of the old sand bottom, sand or quartz, as I have said before, whenever introduced in the puddling furnace, always producing cold-short iron.

The cast iron bottoms are what are called set before using, that is,

some cinder and hammer-slack is thrown in it and melted, or, what is better, a quantity of scrap-iron or old iron is melted on the bottom.

Ilmenite or titanite iron forms a very durable fettling. It is a very infusible material, and answers in some cases, for example, when the iron is very red-short. Mostly, however, it is impossible to use it, on account of its making the iron cold-short.

Other materials are occasionally used for fettling, such as limestone, the rather impure top of the mountain limestone answering the best; it, however, makes the iron very red-short. Roasted tap-cinder, known technically as *bull dog*, is also largely used; the tap-cinder by roasting becoming infusible.

I have entered somewhat minutely into the question of fettling, as upon this point has hinged the question of machine puddling, which has only been recently solved, and in this country it is only a few weeks since that a furnace was started. It is in every way satisfactory in its working.

Several attempts have been made to puddle iron by machinery, and for some time past mechanical rabblers have been attached to puddling furnaces for the purpose of assisting the workman in the heavy labour of stirring the iron; their use has not, however, been very extensive, and they are useless for the purpose of balling the iron up, which is one of the most laborious parts of puddling.

Various inventors have used a revolving chamber so as to puddle the iron mechanically. The first that was attended with any amount of success was that by Mr. Tooth, who used a cylinder made of wrought iron and lined with fire bricks, the cylinder being made to rotate between the fireplace and flue, the flame passing through the cylinder, and the balls being drawn out at the end. The brick lining, however, soon wore away, and the iron was only imperfectly puddled, the ball in the centre still containing some unconverted cast iron.

Mr. Menelaus improved on Mr. Tooth's machine, and, no doubt, succeeded in puddling iron mechanically; the puddling process was most effectually carried out, and was, in my opinion, as complete as any hand puddling I ever saw. His machine differed from Mr. Tooth's in being in the shape of an ellipse, the idea being that whereas in Tooth's machine the iron was simply rolled round, in the elliptical machine, from the unequal diameter of various parts, the action would be to break up the cylindrical mass of iron formed in Tooth's machine, and so submit every portion of the iron to the oxidising action of the cinder and air, and not to leave a core of cast iron in the centre. The ellipse in Menelaus' machine was made movable, and, by means of a pair of trunnions and a crane, it was removed from the furnace, tilted on end, and the lump of iron all in one mass turned out on to a bogie and taken to the hammer.

Mr. Menelaus failed in introducing machine puddling, simply on account of the lining he used; he tried first of all ganister (sand used for lining Bessemer converters) all descriptions of brick, ilmenite, &c., his difficulty was, however, that he could get no lining to stand, and, not only this, all the iron he made was cold-short, and inferior in quality; ilmenite he found to stand the best; it was, however, difficult to fix in the furnace; and, not only this, it made the iron cold-short.

Mr. Dankes' rotatory puddling furnace has been successfully used in America for some time, several works having numerous furnaces constantly at work. The Iron and Steel Institute sent out a Commission to America to report on this machine at the close of last year. Elaborate reports were presented to the above Institute at its last meeting in London, and the Committee appointed report most favourably on it.

A trial furnace has been erected at Messrs. Hopkins, Gilkes, and Co., at Middlesbro', and the trials that have been made with it are so satisfactory, that numerous furnaces are being erected.

Mr. Dankes' machine consists of a revolving cylindrical chamber, made with longitudinal wedge-shaped recesses, which act mechanically in retaining the initial lining in its place. This initial lining may be composed of any ore free from silica, ground up and mixed with lime cream; it is put in like mortar, and, when dried, becomes a refractory and sufficiently coherent material to allow of the fettling being melted upon it, without either melting itself or breaking away from the plates. It is advisable to use an anhydrous ore for mixing with the lime, as when a hydrate is used and the water of combination driven off, the mixture becomes rather crumbly.

Upon the initial lining a quantity of any ore free from silica is melted. For this purpose, ores containing water of combination, may be used, as it is soon driven off. Into the melted bath of ore large solid lumps are thrown, and these being cold, cause the melted ore to set round them, and so fix them firmly, producing a rough internal lining, and thereby affording a greater amount of surface to act upon the iron. It is not only necessary that these lumps should be moderately free from silica and refractory, but also that their texture should be such that they do not crumble by heat; this was found to be the case with ilmenite.

Best tap-cinder answers for this purpose very well, and when iron ores cannot be got free from cinder, there is no doubt that it will pay to oxidize iron-scrap. Mr. Dankes uses scrap iron for this purpose.

The above description is taken from Mr. Snelus's report to the Iron and Steel Institute. In this report he enters fully into the various trials made with English pig iron, and the ores used for fettling in this country that were taken out to America for experiment.



Mr. Dankes in his furnace uses a closed ash-pit, and supplies the necessary air with fan-blast; he also introduces over the fire grate in front of the furnace and above the fuel, nine jets of air, so that the puddler in charge of the machine can regulate the blast, and thus he has complete control over the furnace, increasing the heat when required.

The furnace is a bad melter of pig iron, as it takes a long time and consumes much fuel in using the machine for melting. The pig should be melted in a cupola, or run direct from the blast furnace.

After melting the iron, a jet of water is directed against the lining on the descending side, in order to chill a portion of the cinder and to cause it to be carried under the iron. Mr. Snelus thinks this also has the effect of carrying off sulphur from the cinder, as in Parry's steam finery.

When grey pigs are used, it takes about ten minutes for the boil to commence; with white pig the time is much less, on account of the silicon present in the iron being less, and the boil commences in two minutes after melting. After tapping off the cinder, the cylinder is set revolving, and the fire is urged; the iron begins to boil violently, and the carbon quickly disappears. But little cinder is formed in this part of the process, and most of it is removed with the ball.

Mr. Dankes has an ingenious arrangement consisting of a movable piece or door at the back of the flue; this, on removal, permits the ball to be withdrawn by means of a ball fork worked with a crane, by which the ball is placed on a bogie and carried to the squeezer or hammer.

In Mr. Dankes' machine the puddling is effected entirely by the fettling he uses, the carbon, silicon, and phosphorus being oxidized almost entirely by it, and the cinder introduced. The conversion of pig iron into malleable iron by means of oxides of iron is a very old idea. Dr. Percy proposed it more than 20 years ago; it has been tried in the puddling furnace, but with only partial success, the difficulty always being to bring the iron ore into immediate contact with the molten pig; if used in an ordinary puddling furnace it would simply float on the top. The advantage of using pure oxides of iron and such a material as best tap for fettling a puddling furnace, I have before alluded to; the molten pig washes up against it, and you have in a limited degree the same action as in Dankes' furnace.

The separation of silicon, sulphur, and phosphorus by Mr. Dankes' puddling-machine is more perfect than by hand puddling. Mr. Snelus, in his paper alluded to, gives the analyses of the pig and puddle bar produced, and compares the latter with puddle bar made in the ordinary way, and Mr. Dankes also makes the somewhat astounding assertion that the more silicon and phosphorus the pig contains, the

better is the quality of iron produced, so that what we always considered our enemies are now to be our best friends in iron-making; as far as our experience goes in machine puddling, this view of Mr. Dankes seems to be a correct one.

Mr. Snelus, by an experiment made with silicon and oxide of iron, clearly proved that silicon does reduce oxide of iron to metallic iron, and that it becomes silica. The great advantage of machine-puddled iron will be uniformity of quality in the wrought iron made.

The impurities in the pig being oxidized at the expense of the fettling and cinder, it is clear that the oxides of iron must be converted into metallic iron, and consequently the yield is increased, thus 21·602 lbs. of pig gave of puddle bar 23·112 lbs., allowing 94 per cent. for the iron in the pig, then 1·652 lbs. of iron was reduced from the fettling.

The present machinery in use at iron works is quite unfitted for dealing with such a mass of iron as a ball from Dankes' furnace, the charge used is 600 lbs., the puddle-ball would weigh about 650 lbs. Mr. Dankes has invented a squeezer suitable for such masses of iron, consisting of an excentric grooved roller, with two smaller ones, and a cam to tumble up the iron laterally.

Iron thus produced, after being thoroughly squeezed and re-heated, can be rolled out at once into a rail, or large bar, and will not require, as is the case at present, rolling into puddle-bar, piling, re-heating, and rolling again.

Mr. Spencer, of the West Hartlepool Iron Works, has also invented a revolving puddling machine. The converter is of a rhomboidal form, on two of its opposite sides, having the axes at right angles to the ends or discs, the remaining two sides being parallel to the axis; the ends or discs are made to revolve on rollers by suitable gearing. The sides are fitted with honeycomb recesses to hold the fettling, the discs being honeycombed also for the same purpose.

The fettling used is best tap; it is fitted into the recesses, and fresh tap melted over it. In some experiments made by Mr. Spencer, he found that the silicon and phosphorus were almost completely separated from some Cleveland pig containing over 2 per cent. of phosphorus, having this element reduced in the puddle bar to less than ·10; some of this was probably due to the cinder in the puddle bar.

*Cold-short Iron.*—Iron made from ores containing much phosphorus is always cold-short; thus the character of the Cleveland iron is cold shortness. Cold-short iron is also produced when any siliceous material is used for fettling sand or silica in any form seeming to make iron cold-short, so that generally phosphorus and silicon make iron cold-short.

*Red-short.*—The character of the Welsh iron, and hematite pig, is

red-shortness; red-short iron is always made from ores that are deficient in phosphorus, a little phosphorus from such pigs as the Cleveland producing the best results when mixed with hematite pig, or the purer charcoal irons.

The red-short character of Welsh iron cannot be attributed to the absence of phosphorus; in many instances it is undoubtedly due to the presence of sulphur, although not always; iron may be both red-short and cold-short at the same time. Such iron is the worst possible iron, and is made from iron ores containing a high percentage of sulphur and phosphorus; thus I have found inferior black band, which on analysis gave a high percentage of sulphur and phosphorus, affect materially the quality of the iron, and make it both cold-short and red-short. The exact cause of the production of red-short iron is not always very clear. I believe it to be due in some cases to a deficiency of carbon in the wrought iron; thus the best cable-bolt, the most fibrous and toughest iron, when melted in a clay crucible, and afterwards heated, doubled and welded, is very red-short, on account of the carbon being burnt out by the oxide of iron formed in melting the bar.

*Burnt Iron.*—Mr. Matthieu Williams considers that burnt iron is due to oxygen dissolved in the iron, or rather oxide of iron present in the iron.

I hardly think his experiments are sufficiently conclusive to prove this; he bases them entirely on the behaviour of the iron with dilute 1·20 nitric acid. Now oxide of iron does exist in iron, especially in plates as cinder; frequently in badly manufactured plates it occurs in some quantities. How he can determine the difference between the oxide of iron due to the cinder and that which he considers to cause the burnt iron, I cannot see.

Mr. Matthieu Williams bases all his results on the determination of carbon by Eggertz's process. Now, is this process sufficiently trustworthy to determine minute differences in steel? I think not; that for practical purposes, when used with steel manufactured at the same works, it gives valuable comparative results, I quite agree; but with different steels made by different methods, although I have made most careful experiments, determining by combustion the carbon in my standards, I have been unable to get good practical results.

It would have been more satisfactory if Mr. Williams had first melted his wrought iron and proved that it contained no carbon by combustion; if, then, he had examined the iron after exposure to a high temperature in an oxidizing atmosphere, and then examined it and found oxide of iron, he would have had better grounds for his statement.

I have examined some of the first Bessemer iron made at Dowlais in 1856 by his method. Nearly the whole of the pig introduced in the experimental converter was burnt to cinder, and surely if burnt iron contained



oxygen, this iron should. I have failed to notice the dark colour mentioned by Mr. Williams due to suspended oxide of iron during the dissolving of the iron in 1·20 nitric acid; the experiment has been repeated by my assistant with a like result.

I have also tried the same sample of melted wrought iron upon which I made the experiments alluded to by Mr. Williams, and I have failed to obtain any dark colour or any indications whatever of suspended oxide of iron, the colour of the liquid being a very pale yellowish green; 2·8—2·7—2·5 grains were used in each case.

That burnt iron may absorb oxygen or some other gas when it has been heated to an excessively high temperature is quite possible; but I think it probable that burnt iron may be due simply to the particles or crystals of iron becoming sufficiently soft to arrange themselves in a highly crystalline form, and possibly some gas may remain between the interstices of the crystals. The best fibrous cable iron used for chains, if hammered vigorously for an hour, becomes highly crystalline and brittle, due to a re-arrangement of the particles of the iron; may not burnt iron be due to a similar cause.

By re-heating and re-rolling burnt iron, its crystalline character may in a great measure be converted into a moderately fibrous condition.

In considering the quality of wrought iron and steel, we should, I think, carefully consider the mechanical treatment it has been submitted to in conjunction with the chemical composition of the iron.

### *Steel.*

The time at my disposal will not permit me to enter fully into the composition of steel, and I purpose only considering some points of interest that have lately occupied my attention, more especially as to the occurrence of silicon in steel.

It has always been the general impression that any amount of silicon in steel reduces the quality and seriously impairs its strength. Mr. Snelus, in his paper on the condition of carbon in iron and steel, gives the analyses of brittle Bessemer steel containing silicon and compares it with the analysis of good steel, which contains only a very minute quantity; thus:—

The former	gave silicon	·640,	the latter	·009
„	„	carbon	·550,	„ „
				·490

The former, a steel rail, was broken by a ton monkey falling from a height of 20 to 30 feet, whilst the latter was not broken.

Some time ago I was surprised to find in a sample of Mr. Mushet's so-called titanium steel a large percentage of silicon; the steel was undoubtedly of good quality, and in trying it practically it stood all

the tests that are usually applied to good tool steel. The steel gave on analysis—

Carbon .....	1·283	1·286
Silicium .....	1·343	1·299
Sulphur .....	·074	
Phosphorus .....	·045	
Manganese.....	·480	
Iron.....	97·316	
	<hr/>	
	100·541	

No titanium could be detected.

The siliceous iron made from red ore, charcoal, and sand, was made partly with the object of using it for experiments to ascertain the influence of silicon on steel. Care was taken that all the materials used were as pure as possible.

A mixture of siliceous pig, Spiegeleisen, and shear steel was melted in a small clay pot in a Siemen's furnace. The mixture used consisted of—

Best shear steel .....	1 lb.
Spiegeleisen.....	100 grms.
Siliceous iron .....	800 „

Great difficulty was experienced in melting it, as the clay crucible was enclosed in a larger black lead one; by exposing the clay crucible directly to the action of the gas the steel was melted and with some difficulty poured into a small cast-iron mould.

The steel worked well under the hammer, the edges being particularly sharp. It was drawn out to a bar about  $\frac{3}{4}$  in. square and made into a tool. Unfortunately at the end it was not quite solid; however, by drawing out the other end, a small tool was made from it, and it was used for turning off the skin of cast steel wheels, which is perhaps the most severe test a tool could be submitted to. It stood well, and the edge of the tool turned up slightly, showing that the steel was tough. The steel gave on analysis 2·07 per cent. of silicon.

I regret I am unable to give the Society any details as to the strength of such steel; it was my intention to have made further experiments on this point. It is, however, quite clear that good tool steel may contain over 2 per cent. of silicon; and from the trials made with the steels of which I have given the percentage of silicon and the analysis, I am not disposed to think that either of them is a weak steel; I believe them to be quite as strong as ordinary crucible cast steel used for castings.

I have suggested the use of this siliceous alloy for the purpose of making steel castings more solid. The difficulty with steel castings is

to get them perfectly solid. To attain this it is necessary to use a steel which contains a high percentage of carbon and which is consequently brittle.

Some steel wheels that had failed were sent to me for analysis, to see if there was anything in the steel that would account for their failing.

*Analysis of Steel Wheels (cast).*

	I.	II.	III.
Carbon .....	1·233	1·237	1·203
Silicium .....	·297	·303	·427
Sulphur .....	·022	·017	·032
Phosphorus....	·069	·069	·093
Iron.....	97·544	97·882	97·740
Manganese....	·881	·955	·957
Copper.....	traces	—	—
	<hr/> 100·046	<hr/> 100·463	<hr/> 100·452

Ingot reported to be the same steel from which the wheels were cast—

	IV. Ingot steel.	V. Cast steel wheel.
Carbon .....	·435	·838
Silicium .....	·155	·216
Sulphur .....	·017	·037
Phosphorus .....	·131	·073
Iron .....	99·499	98·794
Manganese.....	·367	·453
Copper .....	traces	—
	<hr/> 100·604	<hr/> 100·411

The analyses given of the steel wheels I and II were from the teeth of wheels that had broken.

Analysis III is a sample of steel from the same works from a pinion wheel.

Sample IV was reported to be the same steel from which the wheels I and II were cast.

Sample V is the analysis of a cast steel wheel from another steel works.

Steel castings have become now almost a necessity for certain parts of machinery where great strength is required, especially for spur, bevel, and pinion wheels.

The great difficulty with steel castings is to make the castings sound, the upper part generally being more or less honeycombed. To



get sound castings, the melters introduce a certain amount of Spiegeleisen to make the steel more fluid. The consequence is that the carbon is made much higher and the wheels more brittle.

All steel castings are annealed, and their strength depends very much upon the care with which this is carried out.

Steel castings having the composition of I, II, and III require more careful annealing, and are more likely to break than sample V, although it is quite possible that steel wheels having the composition of I, II, and III may stand well if very carefully annealed; the composition of sample No. V is, however, very much better.

My impression is that for steel castings it would be advisable to increase the percentage of silicon, and to employ that element to make the steel even more fluid, and consequently obtain greater perfection in casting. I am about to carry out some experiments as to the effect of an admixture of siliceous iron to steel castings, to see to what extent their strength is reduced by adding silicon in various quantities.

Mr. Nees, of York, Pennsylvania, has taken out a patent for making silicon-steel. No details are, however, given as to its character and properties, further than that he uses siliceous magnetic oxide from Heidelberg, York County, Pennsylvania, to make it.

Chromium steel made in America has been tried in this country for a holing awl in a coal-cutting machine; it stood well, and generally the impression was favourable as to its quality. It is stated that the chromium partly or wholly replaces the carbon. In examining the steel I found chromium, although only in small quantity.

Chromium makes excessively hard alloys with iron. I have made alloys containing up to 20 and 30 per cent. of chromium. This alloy was much harder than steel, and dented it easily.

Mr. Henderson, an American in this country, is carrying out a series of experiments with fluor spar. He patents the use of this for puddling and refining iron by mixing it with various mixtures of iron ore, ilmenite, clay, &c. Samples of iron that have been treated by his process, made from pigs containing a high percentage of phosphorus, I have found to be so free from it that the iron is adapted for making steel. The phosphorus I have found reduced to .06 per cent.

Some trials have been made in the Harz with fluor spar in puddling. It is said that a fibrous bar, not at all cold-short, is made from pig containing much phosphorus, and that such iron, when heated in the ordinary way, makes a cold-short iron.

XVIII.—*On the Determination of the Solubilities and Specific Gravities of certain Salts of Sodium and Potassium.*

By DAVID PAGE, M.B. Edinburgh, and A. D. KEIGHTLEY, F.C.S.

THE authors being engaged in the manufacture of nitrate of potassium from the nitrate of sodium and chloride of potassium at an early period after the introduction of this method in England, found it necessary to carry on a series of investigations into the behaviour of these salts when alone or together in solution.

The absence of any trustworthy information in any of the works on technical chemistry, and the discrepant statements collated in Storer's "Dictionary of Chemical Solubilities," induced the authors to extend their experiments, and the results contained in this paper now placed before the Society are given with the hope that from the care and precision exercised in their research, these may be accepted as trustworthy data.

I. The solubilities and densities of saturated solutions of the nitrates and chlorides of sodium and potassium at the temperature of  $15.6^{\circ}$  C.

The salts employed were chemically pure, and accurate thermometers, graduated to  $\frac{1}{10}$ th of a degree, were specially made by Desaga, Universitäts Mechaniker, Heidelberg.

Two modes of solution were adopted:—

*a.* Digestion of the salt in distilled water at a constantly maintained temperature of  $15.6^{\circ}$  C.

*β.* Saturation with the salt of distilled water at  $100^{\circ}$  C., and subsequent cooling down to  $15.6^{\circ}$  C.

The first mode proved the more exact, the numerous control experiments closely agreeing, as the extreme variations show.

The determination by saturation at a higher temperature and subsequent cooling proved that a state of supersaturation obtains less or more in every instance; but in the case of these anhydrous salts this phenomenon cannot be attributed to different degrees of hydration, as in that of sulphate of sodium. The fact that solutions so prepared exhibit a greater density at  $15.6^{\circ}$  C. than those maintained at that temperature from the outset has a probable explanation in what may be termed "the attraction of solution."\*

The excess of salt slowly separates after a lapse of time, and beyond 24 hours the densities attained by both modes correspond.

\* In other words, the indisposition for the salt to change its state by virtue of the attraction of the mass in solution.—D. P.

*Chloride of Sodium.*

Specific gravities of solutions by digestion at—

15° C.	100° C. Cooled down to 15° C.
1204.19	1211.48
1204.03	1206.93
100 parts of water dissolve—	
35.76	36.26
contained in 100 parts of solution—	
26.34	26.61

*Chloride of Potassium.*

Specific gravities of solutions by digestion at—

15° C.	100° C. Cooled down to 15° C.
1171.72	1171.94
1171.45	1171.71
100 parts of water dissolve—	
32.88	33.06
contained in 100 parts of solution—	
24.74	24.84

*Nitrate of Sodium.*

Specific gravities of solutions by digestion at—

15° C.	100° C. Cooled down to 15° C.
1378.15	1378.43
1378.32	1378.17
100 parts of water dissolve—	
84.21	84.69
contained in 100 parts of solution—	
45.71	45.85

*Nitrate of Potassium.*

Specific gravities of solutions by digestion at—

15° C.	100° C. Cooled down to 15° C.
1141.68	1142.25
1141.23	1141.32
100 parts of water dissolve—	
26.04	26.30
contained in 100 parts of solution—	
20.66	20.82
	2 R 2



*Sulphate of Potassium.*

Specific gravity of solution by digestion at 15.6° C.	1176.84
100 parts of water dissolve .....	9.26
100 parts of solution contain .....	8.48

The following table will afford a comparative view of these results. The solubility of one part of salt, deduced from the above experiments, is also shown, and the value of the specific gravities in degrees of Twaddell's hydrometer is attached for technical purposes.

I. Table showing the Specific Gravities and degree of Solubility, by digestion of the salts at a constantly maintained temperature of 15.6° C. = 60.08° F.

	Specific gravity.	Degrees of Twaddell.	Contained in 100 parts saturated solution.	100 parts of water dissolve.	1 part of salt soluble in parts of water.
NaCl ....	1204.03	40.8	26.34	35.76	2.79
KCl.....	1171.10	34.2	24.74	32.88	3.04
NaNO <sub>3</sub> ..	1137.81	75.6	45.71	84.21	1.18
KNO <sub>3</sub> ....	1141.23	28.2	20.66	26.04	3.84
K <sub>2</sub> SO <sub>4</sub> ....	1176.84	35.4	8.48	9.26	10.79

II. Table showing the Specific Gravities and degree of Solubility by saturation at 100° C., and subsequent cooling down to 15.6° C. = 60.08° F.

	Specific gravity.	Degrees of Twaddell.	Contained in 100 parts saturated solution.	100 parts of water dissolve.	1 part of salt soluble in parts of water.
NaCl ....	1206.93	41.4	26.61	36.26	2.75
KCl.....	1171.82	34.4	24.84	33.06	3.02
NaNO <sub>3</sub> ..	1378.43	75.7	45.85	84.69	1.18
KNO <sub>3</sub> ....	1142.25	28.5	20.82	26.30	3.80

*Estimation of the Specific Gravities of the Nitrates and Chlorides of Sodium and Potassium. The Nitrates were rendered anhydrous by careful fusion and the Chlorides by ignition.*

Specific gravities at 15.6° C.

	In absolute alcohol.	In pure oil of turpentine.
KNO <sub>3</sub> .....	2.06	2.06
NaNO <sub>3</sub> .....	2.24	2.25
KCl.....	1.90	1.91
NaCl .....	2.08	2.06

Similar results were attained in another series of estimations, where the salts had been dried over oil of vitriol.

In the last set of experiments, the specific gravities and degrees of solubility of these salts, in presence of each other, were determined, and the results show that, although a solution already saturated by a given salt is still capable of taking up other salts, the degrees of solubility of all present in solution are considerably lessened.

In the analysis of the mixed salts, the potassium, chlorine, and nitric acid were determined directly.

I. *Solution saturated with Chloride of Sodium and Chloride of Potassium at 15·6° C.*

Specific gravity, 1233·74 (46·75° Twaddell).

	100 parts of water dissolve.	100 parts of saturated solution contain.
KCl.....	9·62	13·92
NaCl .....	21·21	30·65

II. *Solution saturated with Nitrate of Sodium and Nitrate of Potassium at 15·6° C.*

Specific gravity, 1478·22 (95·64° Twaddell).

	100 parts of water dissolve.	100 parts of saturated solution contain.
KNO .....	15·29	34·53
NaNO <sub>3</sub> ....	40·39	91·16

III. *Solution saturated with Nitrate of Potassium and Chloride of Sodium at 15·6° C.*

Specific gravity, 1330·92 (66·18° Twaddell).

	100 parts of water dissolve.	100 parts of saturated solution contain.
KNO <sub>3</sub> .....	18·79	32·32
NaCl .....	23·03	39·57

IV. *Solution saturated with Chloride of Sodium, Chloride of Potassium, and Nitrate of Potassium at 15·6° C.*

Specific gravity, 1329·74 (65·95° Twaddell).

	100 parts of water dissolve.	100 parts of saturated solution contain.
KCl.....	·82	1·39
NaCl .....	22·51	38·58
KNO <sub>3</sub> .....	18·33	31·44

V. *Solution saturated with Nitrate of Potassium, Nitrate of Sodium, and Chloride of Sodium at 15.6° C.*

Specific gravity, 1438.63 (87.72° Twaddell).

	100 parts of water dissolve.	100 parts of saturated solution contain.
NaCl .....	12.65	26.44
NaNO <sub>3</sub> ....	25.68	53.68
KNO <sub>3</sub> .....	13.83	28.92

VI. *Solution saturated with Sulphate of Potassium and Chloride of Sodium at 15.6° C.*

Specific gravity, 1241.51 (48.30° Twaddell).

	100 parts of water dissolve.	100 parts of saturated solution contain.
KSO <sub>4</sub> .....	4.99	7.19
NaCl .....	25.52	36.71

VII. *Solution saturated with Sulphate of Potassium, Chloride of Potassium, and Chloride of Sodium at 15.6° C.*

Specific gravity, 1250.42 (50.1° Twaddell).

	100 parts of water dissolve.	100 parts of saturated solution contain.
KSO <sub>4</sub> .....	3.19	4.69
KCl .....	6.88	10.11
NaCl .....	21.88	32.15

XIX.—*On the Influence of Pressure upon Fermentation.* PART I.

By HORACE T. BROWN, F.C.S.

THE following investigation was originally undertaken for the purpose of accurately determining the composition of the gas evolved during the vinous fermentation.

The fact that other gases besides carbonic anhydride are evolved, when glucose splits up under the action of the alcoholic ferment, appears to have been passed unnoticed, or, if observed, has probably been attributed to accidental admixture with atmospheric air. During the research it was found that reduction of atmospheric pressure materially affects the relative quantity, and also the composition of the evolved gases unabsorbed by potash; and these changes in the gaseous products are



accompanied by corresponding alterations in the liquid undergoing fermentation.

In my first experiments malt worts were fermented under ordinary conditions of atmospheric pressure, in a vessel of about 8 litres' capacity, furnished with a gas delivery tube. Precautions were taken to free the liquid from air before the commencement of an experiment, and the fermentation was in most cases allowed to proceed for several hours before any examination of the evolved gas was made. The gas was collected over a strong solution of caustic potash, except where it was required to ascertain the proportion of carbonic anhydride to other gases, in which cases mercury was used.

It was found, after taking every necessary precaution, that during the whole period of fermentation, a certain proportion of gas is evolved, not absorbed by potash. At  $14^{\circ}\text{C.}$ , and in the case of malt-worts, the proportion of the unabsorbed gas to the total amount liberated is found to be about 1 : 3000. A rise in temperature is generally accompanied by a slightly increased evolution of unabsorbed gas.

The analyses of the gas were conducted in an apparatus resembling in general construction that described by Prof. Frankland, in the Journal of this Society for March, 1868. The laboratory tube was, however, much longer and narrower, and was furnished with platinum wires for explosions.

The gases, other than carbonic anhydride, that are evolved during the fermentation of malt worts, under the above mentioned conditions, are found to consist mainly of *nitrogen*, with a small proportion of *hydrogen*, a hydrocarbon, and in some cases nitric oxide.

The following numbers represent the percentage composition of such a mixture :—

Nitrogen .....	92.15
Hydrogen .....	4.85
$\text{C}_n\text{H}_{2n+2}$ .....	1.67
Nitric oxide .....	1.33
	<hr/>
	100.00

It should be remarked that since a somewhat large quantity of potash is required to absorb the carbonic anhydride, it is necessary by a proper disposition of the apparatus to limit the solvent action of the ley upon the gas as much as possible, otherwise little or no hydrogen and hydrocarbon will be detected.

The water used in preparing the malt infusions for the above experiments was ordinary well-water, containing a small quantity of nitrates, from which the nitric oxide was derived by what has been called the nitrous fermentation. It will be seen hereafter that when the fermenting liquid is free from nitrates, not a trace of nitric oxide is evolved.

The hydrocarbon was unfortunately present in too small a quantity in any of the gaseous mixtures yet examined to admit of an accurate determination of its nature. As, however, it is not absorbed by fuming sulphuric acid, it would seem to belong to the  $C_nH_{2n+2}$ , or paraffin group. Whether, however, it is simply marsh-gas, or a mixture of that gas with one or more of its homologues ethane, propane, or quartane, cannot be positively stated; it is hoped, however, that future research may throw some light upon this point.

It might be suspected that the presence of hydrogen would indicate the simultaneous occurrence of the butyric fermentation. This, however, is not the case, for during the performance of certain experiments presently to be described, a method was discovered by which a liquid undergoing fermentation could be made to evolve a considerably greater proportion of hydrogen than when it was fermented under ordinary conditions; and yet in these cases there was no production of butyric acid, which, however, must have been present in a very appreciable quantity had the hydrogen proceeded from that source.

We must then look upon hydrogen as a normal product of the alcoholic fermentation; for in numerous experiments conducted under varying conditions upon malt worts, grape juice, and "Pasteur solutions," by observing proper precautions, I have always been able to detect the presence of that gas amongst the fermentation products.

Liebig in his last paper (*Ann. Chem. Pharm.*, vol. cliii, p. 1) on Fermentation, has suggested that the discovery of hydrogen in small quantities amongst the carbonic anhydride might throw light upon the production of glycerin during fermentation, hinting at the possible production of that body from glucose by the direct fixation of hydrogen according to the formula,

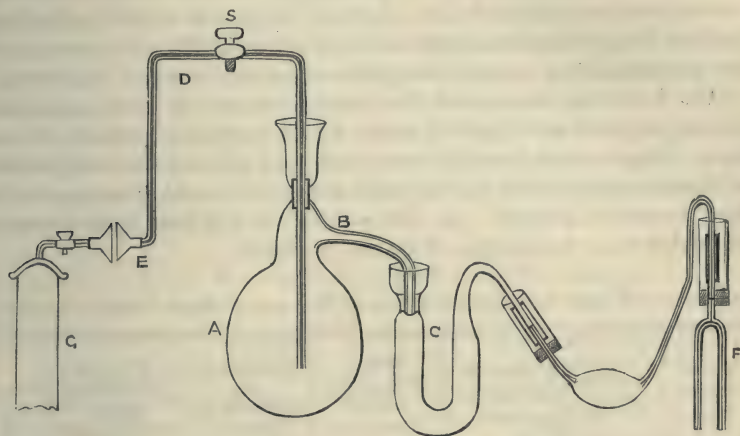


To put this theory to the test of experiment, it will be necessary to estimate the glycerin in liquids which have been fermented under conditions favourable to the production of hydrogen, in which cases there should be a marked excess of that body over the quantity found in the portions of the same liquid fermented under conditions that would yield the maximum amount of hydrogen.

I am, however, at present of opinion that nitrogen is never produced under ordinary conditions, in sufficient quantity to account for the large percentage of sugar, which, according to Pasteur, is converted into glycerin.

In order to understand thoroughly the true sources of the hydrogen and nitrogen, it is necessary to refer to the next series of experiments, which were conducted in an apparatus, the arrangement of which will be readily understood on referring to the accompanying figure. A is

the fermentation vessel, consisting of a flask of about 200 c.c. capacity, partly drawn out at the neck, and with a lateral tube B cemented into



it, by means of which the flask may be connected with a Sprengel's mercury pump, either directly, or, as represented in the figure, by means of a U-tube, C, filled with fragments of caustic potash. Through the drawn-out neck of the flask is inserted a tube D, of about a millimeter bore, bent twice at right angles, and furnished with a well ground stopcock, S. The free end of the tube E has cemented to it one of Regnault's steel caps, for making an air-tight connection with the laboratory tube G of the gas apparatus.

The liquid to be fermented is introduced, together with the ferment, into the flask, the tube D filled with mercury between the steel cap and the stopcock put in position, and all the joints of the apparatus made with mercury or glycerin. If the experiment is to be made under reduced pressure, the potash-tube C is used. As complete a vacuum as possible is now made with the mercury pump, the last traces of air being expelled from the liquid by gentle boiling. When the potash tube is used, this can be readily effected by the heat of the hand alone. When all precautions are taken, there is still a minute quantity of residual air in the apparatus; this is determined previously, and allowed for in all calculations.

A very accurately measured quantity of air or nitrogen (generally from 4 to 8 c.c.) is then passed into the apparatus from the laboratory tube, the tube D being left full of mercury as before.

This admission of air to the flask facilitates the examination of the small quantities of gas proceeding from the fermentation. It also serves another purpose in preventing the continued ebullition of the



liquid in the flask and the consequent wetting of the potash in the U-tube.

After the fermentation has fairly started, it is found that the mercury in the pump remains at almost a constant height, the carbonic anhydride evolved being absorbed as fast as it is produced. When the experiment has proceeded long enough, the gases are pumped out and examined.

The following are some of the results obtained by fermenting malt worts, prepared with distilled water, under varying conditions of pressure. Experiments I and II were conducted without the interposition of the absorption tube; the carbonic anhydride could consequently be here estimated directly. In III and IV it was only approximately estimated from the amount of alcohol produced.

TABLE I.—*Fermentation of 100 c.c. of Malt Wort.*

No. of experiment.	Specific gravity.	Time of fermentation.	Mean pressure in mm. of mercury.	Gas evolved, not absorbed, by potash.	Ratio of unabsorbed gas to total evolved.	Temp. C.
I .....	1057·2	3 days	765	c.c. ·261	$\frac{1}{4500}$	13°
II .....	1047·2	4 "	760	·851	$\frac{1}{4140}$	16°
III .....	1072·0	6 "	440	2·335	$\frac{1}{1400}$	16°
IV .....	1059·2	6 "	390	3·989	$\frac{1}{580}$	17°

TABLE II.—*Percentage composition of Gases evolved during the above Experiments.*

	I.	II.	III.	IV.
N .....	70·11	94·12	35·16	4·83
H .....	2·68	5·88	60·42	90·64
C <sub>n</sub> H <sub>2n+2</sub> .....	27·21	—	4·42	4·53
	100·00	100·00	100·00	100·00

100 c.c. of grape-juice fermented under a pressure of 300 mm. of mercury, and at a mean temperature of 16° C. gave rise to an evolution of gas, of which only  $\frac{1}{9370}$  remained after absorption with potash. The percentage composition of this gas was—

N .....	69·08
H .....	30·92
	100·00

It will be observed from Table I, that the amount of evolved gases unabsorbed by potash is greatly increased by a reduction of atmos-

pheric pressure. This increase is shown by Table II to be mainly due to hydrogen, which is given off in far greater abundance under these conditions. The nitrogen appears on the contrary to decrease with the pressure.

The large percentage of hydrocarbon observed in Expt. I is abnormal. Even here, however, its true nature could not be determined, in consequence of the very small quantity of gas at command.

It is found that an increase of hydrogen in the gaseous products of the alcoholic fermentation is invariably accompanied by an increase in the liquid of acetic acid and aldehyde. This is rendered evident from the following results.

TABLE III.—100 c.c. of Malt Wort Fermented.

	Pressure in mm. of mercury.	Hydrogen evolved c.c.	Acetic acid produced, mm. g.	Reduction of silver oxide by alcoholic distillate.
A ..	755	·211	3·72	Very slight.
B ..	440	1·411	7·60	Slight, but more than in A.
C ..	390	3·616	34·20	Very marked.

The acetic acid was estimated by distilling the liquid, previously freed from alcohol, with a drop of sulphuric acid, and titration of the distillate with  $\frac{1}{10}$  normal soda-solution, the sodium salt being subsequently carefully examined. In experiments A and B the liquids were fermented in the presence of small, accurately measured quantities of atmospheric air. From the total quantity of acetic found in these cases there has been deducted the very small amount corresponding to the oxygen absorbed, on the supposition that the whole of this went to oxidize the alcohol. Experiment C was conducted in a rarefied atmosphere of nitrogen.

It is evident, if acetic acid and aldehyde are, as generally stated, secondary oxidation-products in fermentations, that the necessary oxygen in these cases must have been derived from some substance contained in the liquids experimented upon.

Kekulé (*Deut. Chem. Ges. Ber.* iv, 718) has recently suggested that aldehyde may be produced at the expense of nitrates, these bodies undergoing reduction in consequence. Under some circumstances this may certainly be the case; but that nitrates are not absolutely necessary, any more than free oxygen, for the production of aldehyde, is rendered evident from the results quoted in Table III, where the liquids contained no nitric acid.\* Moreover, I have observed that aldehyde is

\* A simple modification of Schlösing's somewhat complicated method was adopted for examining the liquids for nitrates. Either the worts themselves, or

always present in "Pasteur's solutions," fermented out of contact with the air, and prepared especially with a view to exclude nitrates.

In order to throw some light upon the production of acetic acid and aldehyde, it was necessary that the liquid to be fermented should have a definite and known composition. A "Pasteur's solution" was accordingly prepared of the following substances:—

Cane-sugar .....	10 grms.
Yeast-ash .....	·169 gr.
Ammonium tartrate.....	·118 „
Water.....	100 c.c.

This solution was fermented with a trace of yeast for nineteen days at a pressure of 200 mm. of mercury. The total gas evolved during that period, left unabsorbed by potash, amounted to ·622 c.c., consisting of pure hydrogen. The liquid yielded on distillation 6·6 m.g. of acetic acid, free from butyric acid, and a very marked quantity of aldehyde. It is evident from this experiment, that if the acetic acid was not produced from the tartrate employed, the necessary oxygen for its formation must have been derived either from water or the sugar molecule itself.

A second "Pasteur's solution," in which ammonio-magnesium phosphate was substituted for the tartrate, yielded, on fermentation under a pressure of 50 mm. of mercury, 1·357 c.c. of hydrogen, and 70 m.g. of acetic acid, which in this case contained a trace of butyric acid; more aldehyde being at the same time produced than in the former experiment.

These results seem to point strongly to the fact of there being a decomposition of water during fermentation, the dissociation of the water molecule being favoured by a reduction of external pressure. That the hydrogen evolved is always less in amount than that equivalent to

cold aqueous infusions of the malt from which they were prepared, were introduced, together with a fragment of calcic carbonate, into a flask similar to the one used in fermentation experiments. A vacuum having been made over the liquid, a strongly acid solution of ferrous chloride was passed into the apparatus. When the carbonic anhydride evolved had raised the pressure within the flask nearly to that of the surrounding atmosphere, heat was applied, and the liquid boiled briskly for some minutes. The mercury pump being set in action, the gas was collected in a tube containing a little potash solution.

Malt infusions thus treated, under ordinary circumstances, yielded no nitric oxide. The previous addition of a trace of nitrate could, however, always be readily detected.

I have not yet succeeded in making this method yield good *quantitative* results for very small quantities of nitric acid in the presence of a large excess of complex organic substances, but I have no doubt this may, with proper management, be accomplished.



the oxygen fixed, might be expected *à priori* from what is known of the action of nascent hydrogen on glucose. Petit (*Compt. rend.*, lxxiii, 267—270; *Jour. Chem. Soc.* ix, 897) approaching the subject from a different point, has also arrived at the conclusion that water is actually decomposed during fermentation. The principal facts which he brings forward in support of this opinion, are the conversion by the active ferment of iodine into hydriodic acid, and the oxidation of sulphites to sulphates.

I hope to continue my experiments on these subjects, paying especial attention to the microscopical examination of the liquids fermented under low pressure, with a view to ascertain whether the increased production of acetic acid observed under these circumstances is accompanied by increased propagation of *Mycoderma Aceti*.

A word yet remains to be said on the origin of the nitrogen observed under some circumstances, in the gases of the vinous fermentation. The only possible sources from which this gas may be derived appear to be (1) nitrates, (2) ammonia salts, (3) albuminoids. We have already seen that nitrogen is evolved from solutions containing albuminoids but no nitrates, and that no nitrogen is observed during the fermentation of solutions containing abundance of ammonia salts but no albuminoids. It is evident from these facts that the nitrogen proceeds from the decomposition of albuminoids.

I may state the conclusions I have at present arrived at briefly as follows:—

(1.) That other gases besides carbonic anhydride are invariably evolved during the alcoholic fermentation.

(2.) That for the same liquid, under similar conditions of temperature, the proportion of evolved gas unabsorbed by potash is largely increased by a reduction of atmospheric pressure.

(3.) That the gas always contains hydrogen, and generally a hydrocarbon having the general formula  $C_nH_{2n+2}$ .

(4.) That when albuminoids are present in the liquid, nitrogen is always evolved.

(5.) That the presence of nitrates is indicated by the evolution of nitric oxide.

(6.) That decrease of atmospheric pressure produces an increase in the quantity of hydrogen evolved, and tends to diminish the nitrogen.

(7.) That increase of hydrogen from this cause is always accompanied by an increase of acetic acid and aldehyde in the fermenting liquid.

(8.) That water is decomposed during the vinous fermentation, and that this decomposition is facilitated by a decrease of atmospheric pressure.

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XX.—*On the Electrolysis of Sugar Solutions.* (Preliminary Notice.)

By HORACE T. BROWN, F.C.S.

I HAVE in my last paper shown it to be highly probable that water is decomposed during fermentation. Bearing this in mind, it was thought desirable to subject water to the decomposing action of the electric current in the presence of glucose.

For this purpose a strong solution of invert sugar was prepared. This was acidified slightly with sulphuric acid, and the current from two Bunsen's cells passed through the liquid between platinum terminals.

After the lapse of two hours, the presence of carbonic anhydride could readily be detected in the gas evolved. Twenty-four hours after the commencement of the experiment the electrolytic gas on analysis was found to have the following percentage composition:—

CO <sub>2</sub> .....	14·15
CO .....	3·34
H .....	72·80
O .....	9·71
	<hr/>
	100·00

The liquid was neutralised with soda, and distilled. The perfectly neutral distillate, possessing a slight ethereal odour, produced, on treatment with oxide of silver, a fine mirror of metallic silver, and yielded acetic acid on oxidation. These reactions leave no doubt of the presence in the liquid of considerable quantities of *acetic aldehyde*.

The residue in the retort, redistilled with a little sulphuric acid, gave a strongly acid distillate containing abundance of acetic acid and a little formic acid. It was hoped that alcohol might be produced in this experiment; but although the first distillate gave with iodine and potash the characteristic crystals of iodoform, yet this did not necessarily indicate the presence of alcohol, since Lieben (*Ann. Chem. Pharm.*, vii, Supplement 6, 2 Heft., 226) has shown that the reaction takes place very readily with aldehyde.

Although I have at present no direct experimental proof of the production of alcohol during the electrolysis of glucose solutions, yet I think the composition of the electrolytic gas rather indicates the previous formation of this body, although it probably undergoes immediate oxidation.

I was not aware when I recently commenced the investigation, of which I now present a preliminary notice, that any work had been

done in this direction. I find, however, that Brester (*Archives Néerlandaises des Sciences exactes et naturelles*, 1866, i, 296; *Jahresb. f. Chem.*, 1866, p. 87) in 1866 subjected solutions of cane-sugar, amongst many other substances, to the action of the electric current. He observed the evolution of carbonic anhydride, and also that the electrolysed solution, heated in the water-bath, gave an acid distillate, having reducing properties, but not containing, according to him, formic or acetic acid.

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## XXI.—On the Transformation-products of Starch.

By CORNELIUS O'SULLIVAN.

THE change which starch-paste undergoes in presence of malt-extract (diastase solution) has been investigated by Musculus, Payen, and more recently by Schwarzer.

Musculus (*Ann. Ch. Phys.* [3], iv, 203] states that the solid matter dissolved from starch-paste by the action of diastase at 70° to 75°, or by dilute sulphuric acid under certain conditions, contains sugar and dextrin in the proportion of one molecule of the former to two of the latter, and that with diastase no further reaction takes place, while by continuing the action of sulphuric acid, the dextrin is slowly converted into sugar.

Payen (*Ann. Ch. Phys.* [4], iv, 286) asserts that more than 50 per cent. of the solid matter dissolved by the same reaction is sugar, and says (*Ann. Ch. Phys.* [4], vii, 382) that four samples taken from another operation in the space of 1½ hours contained 17·9 per cent., 20·9 per cent., 25·8 per cent., and 26·03 per cent. sugar on the total matter in solution.

Schwarzer (*J. pr. Chem.* [2], i. 212) agrees with Musculus in finding equivalent quantities of dextrin and sugar in solution, but differs from him in supposing that dextrin is formed first, then sugar, and that the reaction ceases when definite equivalent proportions are produced. He says that when the reaction takes place above 65°, the product always contains less sugar than that produced at a lower temperature; above 65°—70° the proportion of sugar to dextrin is as 1 eq. : 3 eqs.; below 60°, when the principal phase of the reaction is finished, the dextrin and sugar found in solution are in the proportion of 1 eq. : 1 eq. This experimenter considered the change completed when iodine no longer gave any colour. He determined the sugar volumetrically with Fehling's copper solution.



I repeated these experiments, and obtained results agreeing only partially with those given by the chemists named. Certainly below 60°, when the precautions recommended by Schwarzer are taken, the solid matter in solution *frequently* contains 50 per cent., or thereabouts, of sugar. The reaction, however, does not stop here. I find the reducing power becomes constant only when the cuprous oxide precipitated, *weighed* as cupric oxide, represents glucose equal to 65—66 per cent. of the solid matter in solution derived from the starch, the precipitate produced by the malt-extract added being allowed for. The discrepancies between my experiments and those of Schwarzer may be accounted for by two causes.

1st. The difficulty of obtaining, without a foregone conclusion, results nearer than 5 or 6 per cent. by employing the Fehling's solution volumetrically.

2nd. The very slow and gradual increase from 50 per cent. sugar to 65 per cent.

Now the difficulty arises—it also presented itself to Schwarzer—why should not more than 50 per cent., or even 65 per cent., of starch be converted into sugar by the action of diastase? Schwarzer refers to the partial conversion of oxygen into ozone as a parallel phenomenon. I, however, do not think that the one change has any application to the other; and as every fact connected with the transformation of starch is of importance to the manufacture in which I am engaged, I thought it worth the trouble to endeavour to account, in a more satisfactory manner, for this curious point. In pursuit of this object, no better way seemed open to me than to try to isolate the products resulting from the transformation, and study their characters separately. All agree that these products are sugar (the variety of sugar is seldom mentioned) or matter capable of reducing cupric oxide, and dextrin not having that power. The numbers expressing the percentage of sugar, in all investigations on this subject, are calculated on the supposition that the substance in solution which reduces cupric oxide exerts the same reducing power as invert sugar, or dextrose. The dextrin is determined by difference.

There are three principal methods given by which dextrin may be prepared from starch:—

1. By the action of heat on the dry substance.
2. The action of acids, and
3. The action of malt-extract (diastase) on starch-paste.

I shall confine myself to the last two methods.

#### A. *By the Action of Malt-extract.*

100 grams of air-dried starch were stirred up with 300 c.c. water at 40°, and the mixture poured with continued stirring into 2 litres of boil-

ing water. The paste thus formed was allowed to cool to 70° C., and the cold extract from 20 grams of pale malt added to it. Disorganisation immediately set in, the liquid became almost clear; for the first 4 or 5 minutes the filtrate from the solution filtered cold, coloured iodine blue; after some time longer the solution treated in the same way coloured iodine dark reddish-brown, in fact, the colour of concentrated tincture of iodine; at last the cold filtered solution was no longer coloured by iodine. When this stage of the reaction was reached, the solution was boiled for a short time, allowed to cool, and filtered from some insoluble matter which I have invariably found to retain the power of colouring iodine blue. The filtrate was evaporated on the water-bath to 300 c.c., and then precipitated with alcohol. The precipitate was allowed to settle, and the clear supernatant liquid decanted from the insoluble, almost white, waxy mass. This, according to some authors, is dextrin. Biot and Persoz say it can be purified from sugar by dissolving it at least ten times in water and reprecipitating with alcohol, which must not be used in excess. I dissolved and reprecipitated the substance 15 times, and another portion as many as 30 times, the alcohol employed being sp. gr. 0·830,\* but I found in each case that it retained the power of reducing cupric oxide, the lowest reduction corresponding to 8 per cent. dextrose.

### B. *By the Action of Acids.*

100 grams of starch, converted into a paste as described above, were heated with 10 c.c. ordinary sulphuric acid until the solution, filtered cold, no longer coloured iodine. The acid was separated with baryta, and the filtrate evaporated to 300 c.c. The precipitate from this syrup, with alcohol, redissolved, and precipitated 30 times, still retained the power of giving a reduction with cupric oxide equal to 9 per cent. dextrose.

Starch-paste treated in the same way with oxalic acid, the acid being separated with lime, gave the same results, but the transformation was slower.

The question naturally suggested itself, is this body, even after the repeated partial precipitations, still a mixture of dextrin and sugar? or has pure dextrin a reducing power on cupric oxide? An elementary analysis would not settle the point, because the *increase* of hydrogen and *decrease* of carbon, due to the admixture of 8 or 9 per cent. dextrose, could be more or less accounted for by the errors of manipulation; the results would, therefore, not be altogether satisfactory. The action of the body on polarised light seemed to afford some means of explaining the difficulty. The numbers given for the specific rotatory power of dex-

\* This is the strength of the alcohol employed in these experiments.

trin do not agree; in all books it is put as  $[\alpha] = + 138.68^\circ$ ; Béchamp says it is  $[\alpha] = + 176^\circ$ . I determined the specific rotatory power\* of the three substances, the preparation of which is described above, viz., *a*, that obtained by the action of malt-extract; *b*, by the action of sulphuric acid; and *c*, by the action of oxalic acid, with following results:—

<i>a</i>	sp. rot. power	$[\alpha] = + 204^\circ$ .
<i>b</i>	„	$[\alpha] = + 205^\circ$ .
<i>c</i>	„	$[\alpha] = + 204^\circ$ .

The three bodies gave nearly the same reduction with cupric oxide; it equalled—

In <i>a</i> .....	8.8 per cent.
In <i>b</i> .....	8.5 per cent.
And in <i>c</i> .....	9.0 per cent. glucose.

This would seem to indicate that the composition of the substance prepared by the three methods was the same. In another preparation, *d*, however, by the action of dilute sulphuric acid, in which the reaction extended over eight hours, I found the sp. rot. power to be  $[\alpha] = + 198^\circ$ , and the reduction with cupric oxide to be equal to 9.0 per cent. glucose. Either the substance *d* must be a different body from *a*, *b*, and *c*, although the difference in the rotatory power is not great, or the optical activity of the constituent which reduces cupric oxide cannot be the same. This led me to prepare substances having different reducing powers on cupric oxide, by the continued action of sulphuric acid on the body described as *d*, and to determine if the specific rotatory power diminished as the reducing power increased. I found it to be so; but it was not necessary to continue the experiments in this direction, for I observed that the reducing power of the solution could be very considerably diminished by fermentation. I made use of this fact to eliminate the reducing body.

The precipitate produced by alcohol in the syrup obtained by the action of malt-extract on starch-paste, as described above, was dissolved in water; the solution boiled to drive off the alcohol, cooled to  $20^\circ \text{C.}$ , and then 2 per cent. on the matter in solution, of yeast, added to it. Fermentation began in a short time, and in about three days the solution became clear. The specific gravity before fermentation should be 1.090. The clear liquid was filtered to remove the deposited yeast and the filtrate precipitated with alcohol. The precipitate collected to a white, soft, waxy mass, with a lustre more or less silky. This substance was re-dissolved in a small quantity of water, filtered from a little insoluble

\* The optical observations were made with a Soleil by Duboscq. As the mean of six determinations, I found the specific rotatory power of cane-sugar to be  $[\alpha] = + 74^\circ$ ; the extremes being  $+ 74.2^\circ$  and  $+ 73.6^\circ$ . The number usually given is  $+ 73.8^\circ$ .



matter, and reprecipitated; the process was repeated three or four times. The supernatant liquid of the last precipitation was nearly clear; it was poured off and fresh alcohol added; the substance then became gradually brittle, and broke up into a white, apparently semi-crystalline powder. This was washed two or three times with alcohol, thrown on a filter, pressed between folds of blotting-paper and immediately placed under a bell-jar over sulphuric acid. If this precaution be not quickly taken, moisture is absorbed, and the powder again becomes soft and waxy. The body thus obtained, dried in a current of dry air at  $100^{\circ}$ , exerted a reducing power, when boiled for 20 minutes with Fehling's copper solution, only equal to 2 per cent. glucose.

In this way I made eight preparations, viz. :—

3. *e*, *f*, and *g*, from the product of the action of diastase on starch-paste, stopping the transformation by boiling when the colour with iodine was no longer blue, but reddish-brown.

2. *h* and *i* in the same way, stopping the reaction when iodine gives no colour.

1. *j*, from the solution with sulphuric acid, the acid being separated when iodine ceased to give a blue colour, but reddish-brown.

1. *k*, in the same way, when iodine gave no coloration; and

1. *l*, obtained by the action of oxalic acid; coloured by iodine reddish-brown.

I determined the specific rotatory power in each of these preparations, with the following results. The substances were treated with a current of dry air at  $100^{\circ}$  until the weight became constant. This operation takes at least eight hours:—

Substance.	Specific rotatory power.	Per cent. reducing cupric oxide.
<i>e</i> .....	$[\alpha] = + 213.0^{\circ}$	2.03
<i>f</i> .....	$+ 212.0^{\circ}$	2.20
<i>g</i> .....	$+ 212.7^{\circ}$	1.24
<i>h</i> .....	$+ 213.1^{\circ}$	1.20
<i>i</i> .....	$+ 212.7^{\circ}$	1.40
<i>j</i> .....	$+ 213.0^{\circ}$	1.15
<i>k</i> .....	$+ 213.5^{\circ}$	0.80
<i>l</i> .....	$+ 214.0^{\circ}$	1.03

From these determinations I feel justified in concluding that the eight preparations are one and the same body, and coupled with the numbers obtained for *a*, *b*, and *c*, that the body in the pure state does not reduce cupric oxide.

Dextrin in this state is a brittle white powder, showing in some instances shining particles which one would suppose were the faces of crystals, but as under the microscope no trace of crystallisation can

be observed, they must be fracture surfaces. It dissolves very easily in water; if the dehydrated body be employed, with a rise of temperature. In cold alcohol, sp. gr. 0.82, it is not perceptibly soluble; at least the cold alcohol which had been for three days in contact with the dry substance, exerted no action on a ray of polarised light, passed through a layer of it 220 mm. in length. An aqueous solution containing in 100 c. c. 10 grms. dry substance, has a sp. gr. = 1.0385, more correctly, 1.03845, the mean of many determinations, varying between 1.0384 and 1.03855. Its specific rotatory power may be taken  $[\alpha] = + 213^\circ$ . This agrees closely enough with the optical activity  $[\alpha] = + 211^\circ$  of the substance described by Béchamp as *soluble starch* colouring iodine blue.

The three bodies, viz. :—

Soluble starch coloured by iodine blue,

$\alpha$  Dextrin coloured by iodine reddish-brown,

and  $\beta$  Dextrin not coloured by iodine,

are therefore alike in their action on polarised light, and in their activity they in no way correspond with the specific rotatory power  $+ 138.68^\circ$  nor  $+ 176^\circ$  given by Béchamp for dextrin.

Dried over sulphuric acid, its weight becomes constant when it contains 9.5 to 10 per cent. water. This it completely loses in a current of dry air at  $100^\circ$ . Determinations in six different samples gave numbers of which the above are the extremes.  $C_6H_{10}O_5 + H_2O$  contains 10 per cent. water. That no doubt may attach to the composition of the body, I made two elementary analyses, one of  $\alpha$ -dextrin, the other of  $\beta$ -dextrin, both dry, with the following results :—

	$\alpha$ .	$\beta$ .	Theory for $C_6H_{10}O_5$ .
Carbon . . . . .	44.16	44.23	44.44
Hydrogen . . . .	6.44	6.36	6.17

It is unnecessary to remark on those numbers; they are sufficiently near when we consider that the body contains at least 2 per cent. of a substance richer in the elements of water, and consequently poorer in carbon.

Treated with malt-extract, the reducing power of a solution of dextrin gradually increases and becomes constant when the cuprous oxide precipitated, weighed as cupric oxide, is equal to 66 per cent. glucose calculated on the dextrin employed. The specific rotatory power of the matter in solution is then  $[\alpha] = 150^\circ$ , having fallen from  $+ 213^\circ$ .

So far, there is nothing in the character of this body to explain why the change should stop when the reducing power equals 66 per cent. of dextrose. We have consequently to turn to the reducing body, and study its characters.

If we suppose the substance described above as *d* to be dextrose having a specific rotatory power of  $+53^\circ$ , we get for the non-reducing body an angle  $[\alpha] = +212.3^\circ$ . The same angle would evidently be not obtained if the reducing substance in *a*, *b*, and *c* were dextrose. On the supposition that the specific rotatory power of the non-reducing body in this last case was  $+212^\circ$ , that for the reducing substance would be  $+120^\circ$  or thereabouts.

Dubrunfaut (*Ann. Chim. Phys.* [3], xxi, 178) has pointed out a sugar in the product of the action of diastase on starch-paste having a rotatory power three times as great as that of dextrose, viz.:  $[\alpha] = +159.6^\circ$  ( $53.2^\circ \times 3$ ). He says that it is identical with the sugar produced by sulphuric acid in the first stages of the reaction. He also states that it is of the same crystalline habit as dextrose, but less soluble in alcohol than that body.

As shown above by the determinations *a*, *b*, and *c*, the specific rotatory power of the substance which reduces cupric oxide, observed by me, is  $[\alpha] = +120^\circ$ , if that of the non-reducing body be  $+213^\circ$ . This is the case under all circumstances, with the substance giving the greatest amount of reduction as well as with that giving the least.

I have prepared the body described by Dubrunfaut, and have very little doubt that the same body is in my hands as that pointed out by him. Its specific rotatory power is  $[\alpha] = +150^\circ$ , Dubrunfaut's number being  $+159.6^\circ$ . It is much less soluble in alcohol than dextrose, and has apparently the same crystalline habit. I find, however, that only 65 per cent. of it is capable of reducing copper-solution in the same proportion as dextrose. If the substance without action on cupric oxide be dextrin (sp. rot. power  $+213^\circ$ ), the rotatory power of the reducing body would be  $+121^\circ$ , close to the number invariably obtained by me from the active substance. Hence, if the body mentioned by Dubrunfaut be a pure sugar, only 65 per cent. of it acts on cupric acid in the same proportion as glucose, and on the contrary, if it be a mixture of dextrin and sugar, the sugar has not the specific rotatory power given by him, namely, three times that of dextrose  $+159.6^\circ$ , but  $+121^\circ$ .

The following experiments were made with the view of ascertaining whether the substance is a mixture or a simple compound. I may add also its mode of preparation.

100 grams of air-dried malt were mixed with 300 c.c. water at  $40^\circ$ , and the mixture well stirred to diffuse as completely as possible the starch granules through the liquid, and then poured with continual stirring into 2 litres of boiling water. The paste was cooled to  $40^\circ \text{C.}$ , the cold extract from 20 grams of pale malt added to it, and the mixture kept between  $40^\circ$  and  $45^\circ$  for three hours. It was then boiled for some time, cooled, filtered, and the filtrate evaporated at  $80^\circ$ , to 300 c.c. The solid matter in solution, calculated from the specific gravity taking 10



grams in 100 c.c. to be represented by 1.0385, had a specific rotatory power  $[\alpha] = +170^\circ$ . It was the same after evaporation as before boiling: hence these two operations produced no change in the substance. The syrup was boiled for a short time with 2 litres of alcohol, sp. gr. 0.820; on cooling, the clear solution was decanted from the undissolved syrup and put aside in a corked flask. At the end of six days, the sides of the vessel were covered with a crystalline crust. This substance dried at  $100^\circ$  in a current of dry air, had a specific rotatory power  $[\alpha] = +150^\circ$ , and reduced copper solution equal to 65 per cent. glucose.

I made five other preparations in the following manner:—

1. The mother-liquid from the last crystallisation was filtered and set aside. In a week the matter crystallised out was separated.

2. The mother-liquid from the last crystallisation yielded a further crop of crystals.

3. Another portion of starch-paste was treated as described above. The solid matter in solution had a specific rotatory power  $[\alpha] = +166^\circ$ , and a reducing power equal to 51 per cent. glucose. The filtrate from the cold solution was evaporated to 300 c.c., placed on a dialyser over 2 litres of water, and allowed to stand for 20 hours. The solid matter in the diffusate had a specific rotatory power  $= +150$ , and gave a reduction of cuprous oxide equal to 65 per cent. glucose. The syrup obtained by evaporating the diffusates of several experiments yielding the same results as those given here, was treated with sufficient alcohol to dissolve one-half at the boiling temperature. When cold, the clear alcoholic solution was decanted from the bright undissolved syrup and set aside to crystallise. The white crystalline substance formed was removed at the end of a week.

4. A portion of this body was treated with a quantity of alcohol insufficient to dissolve it all, the solution allowed to cool, decanted from the insoluble matter, and set aside to crystallise.

5. The first crystallisation from alcohol was dissolved in water and left to itself over sulphuric acid. In time, the solution became a pasty mass of crystals. These were pressed between filter-paper and again crystallised from alcohol.

The following table shows the numbers obtained on the analysis of the five preparations, 1, 2, 3, 4, and 5, dried at  $100^\circ$  in a current of dry air:—

Subs.	Specific rotatory power.	Per cent. reducing cupric oxide.
1 .....	+ 150·6°	64·4
2 .....	+ 150·6°	65·0
3 .....	+ 149·5°	64·4
4 .....	+ 150·0°	63·9
5 .....	+ 150·6°	65·5

These numbers leave very little doubt as to the identity of the five substances, and when I consider the various treatments they were subjected to in their preparation, I am inclined to conclude that this body is a simple compound, and not a mixture of dextrin and sugar. In further support of this opinion, I may offer the following facts, taking the evidence at present for what it is worth:—

I. The ultimate product of the action of malt-extract on starch-paste below 50°, is a substance having a rotatory power equal to that of this body, when the amount of malt-extract added is allowed for, and reduces the same amount of copper-solution, viz., a quantity equal to about 65 per cent. glucose.

II. No matter what the specific rotatory power of the substance dissolved from starch-paste by the action of malt-extract, the optical activity of the body passing through a dialyser from the syrup left on evaporation is always  $[\alpha] = +150^\circ$ , or thereabouts.

The following are only a few of many observations made, the maximum being + 152°, the minimum + 149°, for the specific rotatory power of the matter in solution in the diffusate, the quantity being calculated from the specific gravity, taking 10 grams in 100 c.c. to be represented by 1·0385:—

The substance in—

1st diffusate, sp. rot. power =	+ 150°.
2nd           "           "	= + 152°.
3rd           "           "	= + 149·8°.
4th           "           "	= + 149·8°.
5th           "           "	= + 149°.
6th           "           "	= + 151°.

III. If the substance were a mixture of one-third dextrin and two-thirds sugar, as the reduction with cupric oxide would seem to indicate, it would contain—

Carbon.....	41·47 per cent.
Hydrogen .....	6·49       "

Combustions of the preparations described as 2 and 3, above, dried in a current of dry air at 100°, gave the following results:—

	2.	3.
Carbon .....	41·97 per cent.	42·02 per cent.
Hydrogen .....	6·48     ,,	6·50     ,,

The theory for a sugar isomeric with cane-sugar or with lactose, viz.,  $C_{12}H_{22}O_{11}$ , is—

Carbon.....	42·10 per cent.
Hydrogen .....	6·43     ,,

I think that this, coupled with the facts before stated, leaves very little doubt as to the character and composition of the body under consideration. That it reduces only  $\frac{2}{3}$  as much cupric oxide as glucose, is no reason for considering it to be a mixture. Lactose, a well-defined crystallised body, reduces only  $\frac{7}{10}$  (a quantity not far removed from  $\frac{6}{9}$ ) as much cupric oxide as dextrose, and is isomeric with the substance here described, as far, at least, as the elementary analysis can prove it to be so.

If, then, this body be a simple sugar, and I submit that the evidence is altogether in favour of the supposition, we have at once an explanation of the difficulty which it was the object of this investigation to clear up. This sugar, which, following Dubrunfaut, we shall call *maltose*, is the end-product of the action of malt-extract on starch-paste. It is converted, by the continued action of acids, into dextrose.

There are many points of interest connected with this body; I am at present engaged in an examination of them.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
BRITISH AND FOREIGN JOURNALS.

Physical Chemistry.

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**Use of Secondary Currents for Accumulating and Transforming the Effects of the Galvanic Battery.** By M. PLANTÉ (*Compt. rend.*, lxxiv, 592—595).

THE secondary currents caused by galvanic polarisation being very intense, on account of the very short time in which they discharge the energy absorbed by the electrodes, furnish a means of accumulating and transforming the electrical energy of the galvanic battery. The author has investigated what proportion of the energy is lost whilst the secondary battery receives its charge.

A very efficient battery is formed by lead plates of about half a meter square. When such plates are used as electrodes for the first time, the one becomes superficially oxidised, whilst hydrogen is disengaged at the other, and when the current is reversed, the surface of the first plate is reduced, whilst that of the other is oxidised.

After the current has passed several times in opposite directions, the plates are more readily acted upon, and at last are capable of absorbing the current of a couple of ordinary Grove's or Bunsen's cells so completely for about six or eight minutes, that no disengagement of gas is perceptible at either of them; the appearance of gas-bubbles after this time indicates the moment at which the plates have received the full charge they are capable of absorbing.

In order to compare the effects of the current obtained by connecting the charged electrodes with those of the primary current, the latter was made to traverse a voltameter containing solution of cupric sulphate, and the copper, which, whilst the secondary battery was being charged, was deposited on the negative electrode, was weighed. In the next place the secondary current obtained by discharging the lead electrodes was passed through a voltameter, and the weight of copper precipitated by it was also determined. By comparing the weights of the two deposits it was found that, of the force required to charge the secondary battery, not less than about 88 or 89 per cent. are absorbed by the lead electrodes, to be given out again as a secondary current.

It appears, however, that secondary batteries with lead plates, constructed to produce effects of tension, do not return the electricity spent upon them, as completely as those which are constructed to produce effects of quantity.

R. S.

**The Spectrum of the Solar Corona.** By M. JANSSEN (Compt. rend., lxxiv, 175).

THE spectrum of the corona, seen during the eclipse of December 12, 1871, exhibited the bright hydrogen lines characteristic of the protuberances, together with a green line, previously observed in the eclipses of 1869 and 1870, and others of inferior brightness; also the dark lines of the ordinary solar spectrum, especially the line D. These facts show that the corona is of solar origin; they demonstrate, indeed, the existence of an extremely rare hydrogen atmosphere, extending from the sun to a much greater distance than the chromosphere or the protuberances.

H. W.

**Action of Chromic Acid upon Carbonic Oxide, Hydrogen, Marsh Gas, and Ethylene.** By E. LUDWIG (Ann. Chem. Pharm., clxii, 47—53).

CHROMIC acid is capable of oxidising carbonic oxide; this oxidation can be slowly but completely accomplished by introducing a ball of gypsum soaked with a solution of chromic acid into carbonic oxide over mercury. The reaction is accelerated by concentration of the liquid, and by a higher temperature. For a lecture demonstration, the purified carbonic oxide is passed, first through lime-water, which is not affected by it, then through about six U-shaped tubes filled with pumice-stone which has been moistened with concentrated chromic acid solution, then again through lime-water, which, in the course of about five or ten minutes, is rendered distinctly turbid by the carbonic acid formed.

Hydrogen is likewise oxidised by chromic acid, as is seen from the results of the following experiments, in which a gypsum ball steeped in concentrated chromic acid solution had been introduced into hydrogen over mercury.

	c.c.	Pressure.	Temp.
Original volume of the gas .....	35.8	6.703	17°C.
Volume after 15 hours' action of the chromic acid.	29.0	0.676	16.9°
"        19        "        "        "        "	27.0	0.668	17.1°
"        26        "        "        "        "	23.75	0.655	17.4°
"        65        "        "        "        "	7.0	0.588	18.2°
"        86        "        "        "        "	0.0	—	—

When, however, the chromic acid solution is diluted, the oxidation proceeds very slowly; for instance, a solution prepared by mixing the saturated acid solution with its own volume of water, had oxidised, after 31 hours' action upon 38.5 c.c., not more than 0.5 c.c.; if the saturated solution is mixed with twice its volume of water it produces in hydrogen gas a perceptible diminution of volume only after several days.

*Marsh-gas* withstands the action, not only of the dilute, but even of the concentrated solution of chromic acid.

*Ethylene* is completely oxidised to carbonic acid and water when heated with concentrated chromic acid solution in sealed tubes; but at

ordinary temperatures intermediate products (formic acid, and perhaps also acetic acid) are likewise formed. With dilute solutions the action is very slow, and the oxidation still less complete.

R. S.

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**Temperature Constants.** By S. SUBIÉ (Wien. Anzeig, 1872, 26 ; Chem. Centr., 1872, 177).

THE author shows, by calculation from Joule's experiments, that the working force of the progressive motion of the individual molecules of a gas corresponding to the unit of temperature is the same for all gases. At a given pressure and temperature, gases contain equal numbers of molecules in the unit of volume. The molecules contained in the volume of 1 kilogram of hydrogen, or in an equal volume of any other gas, at the same pressure and temperature, receive, by a rise of temperature equal to  $1^{\circ}$ , an increase of working force of progressive motion amounting to 636 kilogram-meters, whilst in expansion under constant pressure, external work is performed equivalent to 424 kilogram-meters.

The conversion leads to the calculation of the constants of Gay-Lussac and Mariotte's laws, of the velocity of the gas-molecules, and of the mechanical equivalent of heat.

H. W.

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**Conduction of Heat in Gases.** By STEFAN (Wien. Anzeig, 1872, 42 ; Chem. Centr., 1872, 177).

THIS investigation was conducted by two methods. In the one, air enclosed in cylinders was either warmed from above or cooled from below. The enclosed air itself formed the thermometric substance. The mean temperature at each instant could be determined by manometric measurement. The numbers calculated for the conducting power in these experiments come out too small or too large, according as the walls of the vessel conduct more slowly or more quickly than the air. The first case occurs when the walls are of glass or of iron, the last when they are of zinc, whence it appears that air, as a conductor of heat, stands between iron and zinc.

In the second mode of experimenting, an enclosed mass of air was uniformly warmed or cooled on all sides. In the first experiments spherical air-thermometers of copper plate were employed, but the values of the conducting power calculated from these experiments were too large, on account of the influence of currents. The last experiments were made with double-walled thermometers of brass or copper plate, the space between the metallic envelopes being filled by the gas under examination. The values obtained with different apparatus thus constructed agreed very nearly with one another. The conducting power of air was found to be 0.000056 (centimeter ; second ; gram), which is nearly 20,000 times less than that of copper, and 3,400 times less than that of iron. The value calculated by Maxwell from the dynamical theory of gases is 0.000055. The experiments confirm the conclusion deduced from the dynamical theory of gases, that the conducting power of a gas is independent of its density, also the conclusion deduced by



Maxwell from the same theory, that the conducting power of hydrogen is seven times as great as that of air. The dynamical theory of gases may, therefore, be regarded as one of the best established among physical theories.

H. W.

**The Specific Heat of Carbon.** By H. F. WEBER (Deut. Chem. Ges. Ber., v, 303—309).

THE numbers found by different observers for the specific heat of the allotropic modifications of carbon agree, as the following table shows, so little with each other, that their difference cannot be explained by the different methods of observation, or by the impurities of the substances employed.

Observer.	Charcoal.	Gas carbon.	Natural graphite.	Blast furnace graphite.	Diamond.	Interval of temperature.
Regnault.....	0·2415	0·2036	0·2019	0·1970	0·1469	8°—98°
De la Rive and Marcet	0·2009	—	—	—	0·1146	3°—14°
Kopp.....	—	0·185	0·174	0·165	—	22°—52°
Wüllner and Bettendorf..... }	—	0·2006	0·1919	0·1921	0·1452	22°—70°

This table is, however, in accordance with the following law, which the author has now established by direct experiments. The specific heat of carbon increases with the temperature far more rapidly than that of any other substance; for example, the specific heat of the diamond becomes three times as great when the temperature rises from 0° to 200°.

The specific heat of the diamond was determined for twelve different temperatures at about equal intervals between 0° and 200°, and it was found that if the mean specific heat between 0° and the temperature  $t$  is denoted by  $C_{0-t}$ , it can for any temperature  $t$  be calculated by the formula—

$$C_{0-t} = 0\cdot0947 + 0\cdot000497 t - 0\cdot00000012 t^2.$$

The integral of this, which may be called  $\gamma_t$ , furnishes the specific heat at any definite temperature  $t$ .

$$\gamma_t = 0\cdot0947 t + 0\cdot000994 t^2 - 0\cdot00000036 t^3.$$

From this would follow for—

0°.....	$\gamma = 0\cdot0947$
50°.....	$\gamma = 0\cdot1435$
100°.....	$\gamma = 0\cdot1905$
150°.....	$\gamma = 0\cdot2357$
200°.....	$\gamma = 0\cdot2791$

The specific heat of graphite having been found = 0·1439 between

$0^\circ$  and  $34^\circ$ , and  $= 0.1967$  between  $0^\circ$  and  $100^\circ$ , its mean specific heat between  $0^\circ$  and any temperature  $t$  can be calculated from the formula—

$$C_{0-t} = 0.1167 + 0.0008 t,$$

and its specific heat at any definite temperature  $t$  from—

$$\gamma_t = 0.1167 + 0.0016 t.$$

De la Rive and Marcet had found for charcoal—

$$C_{8-14^\circ} = 0.2009,$$

and Regnault—

$$C_{8-98^\circ} = 0.2415.$$

from which results it would appear that the porous modifications of carbon behave in the same way as graphite and diamond.

These results are considered as a strong argument against the law of Dulong and Petit, which would be worth very little if it depended essentially upon temperature.

The author proposes to examine the specific heat of the diamond at temperatures between  $-100^\circ$  and  $0^\circ$ .

R. S.

### Heat of Formation of the Oxygen-compounds of Nitrogen.

By M. BERTHELOT (Compt. rend., lxxiv, 1045—1048).

THE great difference of the following results—

		Heat-units.
$\text{NO}_2 + \text{O}_3 + \text{HO} + n\text{Aq}$	$= \text{NO}_6\text{H}$ (diluted)	$= +36.5$ (Thomsen)
		$= +20.7$ (Favre)
$\text{NO}_2 + \text{O} + \text{HO} + n\text{Aq}$	$= \text{NO}_4\text{H}$ (diluted)	$= +18.2$ (Thomsen)
		$= -6.6$ (Favre)
$\text{NO}_4(\text{diluted}) + \text{O}_2$	$= \text{NO}_6\text{H}$ (diluted)	$= +18.3$ (Thomsen)
		$= +27.7$ (Favre)
$\text{NO}_4(\text{gaseous}) + \text{O} + \text{HO} + n\text{Aq}$	$= \text{NO}_6\text{H}$ (diluted)	$= +16.9$ (Thomsen)
		$= +33.5$ (Troost and Hautefeuille),

cannot, according to the author's opinion, be attributed solely to the difference of the methods and apparatus employed by the different observers, but is more probably due to the fact that some of the above reactions are by no means so sharply defined as they are generally supposed to be; it would also appear that the peculiar physical properties of what is generally called the vapour of nitrous and hyponitrous acids can scarcely be considered as those of completely formed and definite compounds.

The author remarks further that chemical reactions cannot, with regard to their heat-effects, be compared with each other, unless the elements between which they take place are in the same physical conditions with regard to the state of aggregation, temperature, &c., and he thinks that, if this rule had been observed, the apparent similarity of

the heat-effects which Thomsen\* believes that he has discovered between different chemical reactions would, in many cases at least, disappear.

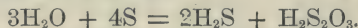
R. S.

**The Drying of Gases.** By JACOB MYERS (Deut. Chem. Ges. Ber., v, 259—264).

IN the course of experiments in which sulphurous anhydride was passed over boiling sulphur, the author observed, on shaking up some water in the receiver in which the distilled sulphur had been collected, a constant formation of pentathionic acid. This could be ascribed to no other source than the action of the sulphurous anhydride upon hydrogen sulphide, resulting from the decomposition by the boiling sulphur of moisture retained in the gas. When carbonic anhydride or nitrogen was substituted for the sulphurous anhydride, no pentathionic was produced, but hydrogen sulphide was readily detected.

The gases thus operated upon had been passed through a long chloride of calcium tube, through a wash-bottle of pure sulphuric acid, and over glass wetted with sulphuric acid. The same results were obtained even when phosphoric anhydride was employed. Hence it appears that gases dried by means of the usual desiccating agents still retain a certain amount of water.

By experiments which have already been published, the author has established the fact that water-vapour is decomposed by boiling sulphur according to the following equation:—



Upon this reaction he finds a process by which the amount of water contained in a given volume of carefully dried gas may be estimated.

From experiments made with nitrogen gas, he finds this amount to be about .00132 gram of water per litre of gas.

W. A. T.

**Lecture Experiments.** By FERD. FISCHER (Deut. Chem. Ges. Ber., v, 264).

IN order to show the force with which the diffusion of gases operates through porous septa, the following apparatus is employed. The open end of a porous cylindrical battery-cell is cemented to a funnel, the neck of which is attached to a vertical glass tube 1,000 mm. long. The lower extremity of this glass tube passes through a cork, which is fitted to the neck of the bottle containing a coloured liquid. Through the same cork passes a short tube, the end of which is drawn out to a point. Both tubes dip into the liquid. If now such a gas as carbonic anhydride is brought into a bell-jar inverted over the porous cell, the liquid rises in the long tube from the bottle below. If a brisk stream of hydrogen be substituted for the carbonic anhydride in the bell-jar, a stream of liquid 1,500 mm. high is at once projected through the short tube into the air.

By the use of a similar apparatus, the specific gravities of gases may be compared and exhibited.

W. A. T.

\* See pp. 215, 457 of this volume.



## Inorganic Chemistry.

### Reaction of the Lead-chamber Crystals with Water. By C. RAMMELSBURG (Deut. Chem. Ges. Ber., v, 310—316).

THE author first gives an historical sketch of the views held by former observers on the constitution of these crystals, and goes on to describe some experiments on their behaviour to water, which, at his suggestion, had been undertaken by Dr. Philipp. It was found that on treatment of the crystals with water, nearly the fourth part of the nitrogen contained in them was evolved as nitric oxide. The aqueous solution was saturated with barium carbonate, filtered and evaporated, and yielded a mixture of barium nitrate and nitrite, the analysis of which showed that 100 parts of crystals furnish 6.38 pts.  $\text{N}_2\text{O}_5$  and 20.47 pts.  $\text{N}_2\text{O}_3$ . From this it can be calculated that on decomposition with water—

	22	p. c. of the total nitrogen is evolved as nitric oxide,
whilst {	14	" " " remains in solution as nitric acid,
	64	" " " " " nitrous acid.

Considering that the nitric oxide and nitric acid are produced by the action of water upon nitrous acid in the proportion of  $\text{HNO}_3 : 2\text{NO}$ , it is probable that the nitrogen-products of the decomposition bear to each other the proportion which would be required for the formation of  $4\text{NO}$ ,  $\text{N}_2\text{O}_5$ , and  $5\text{N}_2\text{O}_3$ , or that

$\frac{1}{4}$	of the total nitrogen goes to form nitric oxide,
$\frac{1}{8}$	" " " nitric acid,
$\frac{5}{8}$	" " " nitrous acid.

In order to examine what the proportion of the nitric and nitrous acids would be at higher temperatures, the aqueous solution of the crystals was submitted to distillation, which was continued until half the liquid had gone over; it was then found, after neutralisation with barium carbonate, that the salts of the residual portion contained 82 p. c. of nitrate and 18 p. c. of nitrite, and those of the distillate portion contained 88 p. c. of nitrate and 12 p. c. of nitrite.

This experiment also shows that the solution of the crystals contains so much nitrous acid that it cannot be driven out, even by long-continued boiling.

R. S.

### The presence of Selenium in Sulphuric Acid of French Manufacture. By J. PERSONNE (Compt. rend., lxxiv, 1199).

THE rarity of the occurrence of selenium as an impurity in sulphuric acid induced the author to publish the following note respecting the presence of this metalloïd in certain samples of vitriol manufactured in the Department of the Seine.

Its presence was first suspected from the fact that, on the addition of crystals of ferrous sulphate to the pure distilled acid, a brownish

coloration was produced, similar to the reaction which would ensue were nitrous compounds present; and further, that when the acid was used for the preparation of hydrochloric acid, the distillate, having first acquired a deep yellow colour, gradually deposited a red powder. The examination of this coloured deposit led to the detection of selenium. The selenium was afterwards separated from the vitriol, by diluting the latter with four times its volume of water and adding a solution of sulphurous acid. The precipitate thus produced was then taken up by agitating the liquid with carbon disulphide, and the selenium finally recovered from the solvent by evaporation. In this manner 0.2 gram of selenium was obtained from three litres of sulphuric acid.

The author is still in doubt respecting the origin of the pyrites from which this sulphuric acid was manufactured, but expects shortly to be able to offer some satisfactory information upon this important point.

J. W.

M. Lamy (*Compt. rend.*, lxxiv, 1285) states that the occurrence of selenium in sulphuric acid of French manufacture was observed by Kuhlmann and himself ten years ago; and M. Scheurer-Kestner (*ibid.*, 1286) says that the same fact was noticed by himself in two papers, published in 1868 and 1870, in the *Bulletin de la Société Chimique de Paris*.

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**Luminosity of Iodine Vapour.** By G. SALET (*Compt. rend.*, lxxiv, 1249).

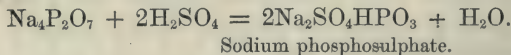
IODINE vapour transmitted through a glass tube heated to a temperature just below redness, becomes self-luminous, giving off light of a red colour with a continuous spectrum.

C. G. S.

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**Transformations of Pyrophosphates.** By PRINVAULT (*Compt. rend.*, lxxiv, 1249—1252).

WHEN sodium pyrophosphate is fused with one equivalent of boric acid, a phosphoborate of sodium is produced, which, by the action of water or alcohol is decomposed into boric acid and ordinary sodium phosphate. If the pyrophosphate be heated with oil of vitriol till vapours of sulphuric acid are no longer evolved, and the product be then dissolved in water acidulated with phosphoric acid, the solution on evaporation yields brilliant plates of a salt having the constitution  $\text{Na}_2\text{SO}_4\cdot\text{HPO}_3 + \text{H}_2\text{O}$ .



An acid phosphate will give a similar result. The new salt is permanent in air. It loses one molecule of water at  $200^\circ$ , and the second only at a red heat, when it is decomposed into sulphuric acid and pyro-

phosphate. Pure water resolves it into phosphoric acid and a sulphate.

On treating metaphosphoric acid with two equivalents of sulphuric acid, a syrupy uncrystallisable liquid is produced, decomposed instantly by water into orthophosphoric and sulphuric acid. The solution is no longer precipitated by albumin. Hence we may conclude that a double acid, corresponding to sodium phosphosulphate, has been formed.

C. G. S.

**Crystallisation of Sodium Hydrate.** By KLAS LINDROTH (Chem. Centr., 1872, 147).

A VERY impure solution of caustic soda, sp. gr. 1.375, gave a large crop of well-defined, perfectly pure crystals, on being cooled to  $-22^{\circ}$ .

The author suggests the application of this *pure* sodium hydrate to the economic preparation of metallic sodium.

M. M. P. M.

**Presence of Calcium Iodate in Sea-Water.** By E. SONSTADT (Chem. News, xxv, 196—198).

THE inference respecting the state of oxidation of the iodine contained in sea-water was based in the first instance upon the result of a series of experiments, the details of which are not given in the original paper, but which led the author to conclude that an iodide cannot exist in an alkaline solution, freely exposed to the air, without becoming rapidly converted into iodate. If such be the case, it is reasonable to infer that the iodine present in sea-water is in the form of iodate, since the conditions under which it exists in that liquid come within the range of the conditions originally submitted to experiment.

The following reactions are considered to prove satisfactorily the accuracy of this assumption:—

Pure sea-water, collected at some distance from land, gives no iodine coloration when acidified and shaken with carbon disulphide; but if a very small quantity of solution of sulphurous acid or ferrous sulphate be first added to reduce the iodic acid, and the liquid be subsequently acidified with dilute sulphuric acid and agitated with carbon disulphide, a recognisable iodine coloration is obtained, even when 100 c.c. of water only are taken.

As a qualitative test for the presence of iodine, the following method of operating is still more accurate:—

200 c.c. of the water to be examined are first mixed with a few drops of a slightly alkaline solution of sodium sulphite, then 2 or 3 c.c. of a saturated solution of silver acetate added, and lastly about one-fourth of the volume of the liquid of strong hydrochloric acid free from chlorine. The liquid is left at rest for a short time, then filtered, and the precipitate washed with dilute hydrochloric acid and distilled water. The filter and precipitate are moistened with a strong solution of caustic soda, and heated in a covered crucible to low redness for a few minutes. After cooling, water is added, the solution filtered, and the filtrate, strongly acidified with dilute sulphuric acid, is shaken up



with carbon disulphide and sufficient very dilute chlorine-water to develop the iodine reaction. The evidence of the presence of iodine is instantly manifest.

As an additional result of the experiments above alluded to, the author finds that the iodates are readily decomposed by putrescent organic matter; it is possible, therefore, if the sea-water to be tested be collected at a spot where it is liable to be contaminated with sewage, that it will give the iodine coloration with disulphide, even without the previous addition of sulphurous acid or ferrous sulphate. One or two samples taken near the shore were found, when fresh, to give no iodine reaction treated with carbon disulphide. In a few days, however, their condition changed; they contained free iodine, and retained scarcely a trace of the original iodate.

Up to the present time the author has been unsuccessful in making a quantitative determination of the iodine.

In continuation of this subject (*Chem. News*, xxv, 231 and 241), the author observes, that if the trifling precipitate produced in sea-water by the addition of a very small quantity of ferrous sulphate be carefully collected and examined, it will be found to contain iodine: also, that the precipitate is readily soluble in excess of the precipitant, with reduction of the iodic acid. These facts he considers as strong presumptive evidence that the precipitate consists mainly of ferrous iodate. It was found, however, impossible to throw down the whole of the iodine in this manner, but the precipitate which contained the largest quantity of iodine was obtained when the proportion of 3 milligrams of ferrous sulphate was employed to 1 litre of the water.

Again, the presence of iodic acid in sea-water may be further proved by fractional precipitation with barium chloride, the last portion precipitated carrying down with it nearly the whole of the iodic acid as sparingly soluble barium iodate. This iodate is somewhat soluble both in solutions of barium and sodium chloride, but may be readily detected in the precipitate by decomposing it with solution of potassium sulphate and examining the filtrate in a suitable manner. For this latter purpose the following method is recommended, which is also applicable for the direct examination of sea-water. The solution of the iodate is first acidulated with a few drops of hydrochloric acid, and then a small piece of magnesium wire is added. An instantaneous separation of iodine ensues, which may be shown in the usual way by agitation with a drop of carbon disulphide. The reaction with magnesium is not only very delicate, but is more persistent than with other reagents.

After many failures to effect satisfactorily the quantitative estimation of the iodine, the analysis was at last successfully accomplished by operating in the following manner:—

500 c.c. of water were taken, and the iodate reduced by the addition of a small quantity of solution of arsenious anhydride in hydrochloric acid; a few milligrams of copper sulphate were then added, the whole evaporated to dryness, and the residue gently dried. The latter was dissolved in the smallest possible quantity of water, and the insoluble cuprous iodide brought upon a filter and washed. The iodine was

finally estimated by igniting the filter with sodium hydrate and subsequently titrating the acidulated solution of sodium iodide with very dilute chlorine-water and carbon disulphide.

The results of the author's analyses are, for the sake of uniformity, reduced to 100 c.c., and the iodine returned as potassium iodide.

(1.)	100 c.c. sea-water	0.000229	KI.
(2.)	" "	0.000203	"
(3.)	" "	0.000236	"
(4.)	" "	0.000330	"
(5.)	" "	0.000277	"

These experiments show that 1 part of calcium iodate is contained in 250,000 parts of sea-water. A cubic mile of sea-water therefore contains about 17,000 tons of calcium iodate, or 11,072 tons of iodine.

J. W.

**Preparation of Barium Chlorate.** By G. WIDEMANN (Arch. Pharm. [2], cxliv, 66).

A MIXTURE of 1 mol. crystallised aluminium sulphate, 1 mol. sulphuric acid, and 2 mols. potassium chlorate is heated with a quantity of water, sufficient to give it a thin, pasty consistence. Crystallised potash-alum then separates on cooling, while chloric acid remains dissolved. A four-fold volume of water is then added, and the liquid, after filtration, is neutralised with baryta-water, whereupon barium sulphate separates out, together with a little more alum. The liquid is again filtered, the greater part of the alcohol removed, and the liquid, after a second filtration, is evaporated to the crystallising point.

H. W.

**The Sulphides of Arsenic.** By L. F. NILSSON (Ofv. af. Vet. Ak. Forh., 1871, 303; Deut. Chem. Ges. Ber., iv, 989).

FROM a careful examination of the older statements respecting these bodies, the author infers that there are but three definite sulphides of arsenic,  $\text{As}_2\text{S}_2$ ,  $\text{As}_2\text{S}_3$ , and  $\text{As}_2\text{S}_5$ , the black sulphide  $\text{As}_2\text{S}_6$ , described by Berzelius, and the higher sulphides,  $\text{As}_2\text{S}_{10}$ , and  $\text{As}_2\text{S}_{12}$ , being merely mixtures.

The *bisulphide*,  $\text{As}_2\text{S}_2$ , does not possess the power of forming salts, as stated by Berzelius.

*Trisulphide* or *Arsenious sulphide*,  $\text{As}_2\text{S}_3$ .—Alkaline sulphydrates, saturated under ordinary circumstances with the trisulphide, yield, for the most part, brown, amorphous compounds, having the general formula,  $\text{R}_2\text{S} \cdot \text{As}_2\text{S}_3 + x \text{ aq.}$  Strontium alone yielded a bibasic salt. In a vacuum, on the other hand, larger quantities of hydrogen sulphide are driven off, and well crystallised salts of a more basic character are often obtained, the sulphides of barium and strontium yielding the salts,  $2\text{R}''\text{S} \cdot \text{As}_2\text{S}_3$  and  $3\text{R}''\text{S} \cdot \text{As}_2\text{S}_3$ , and calcium sulphide forming the salt  $7\text{CaS} \cdot \text{As}_2\text{S}_3 + 25 \text{ aq.}$ —In the case of the true alkaline sulphydrates, the increased elimination of hydrogen sulphide is accompanied by a totally different reaction. With the sulphydrates of potassium and

sodium, metallic arsenic is separated, and a salt of arsenic sulphide,  $3R_2S.As_2S_5 + x \text{ aq.}$ , is formed. Ammonium sulphhydrate,  $(NH_4)_2S.H_2S$ , forms with arsenious sulphide, under all circumstances, the salt  $(NH_4)_2S.3As_2S_3$ ; rarefaction of the air merely causes the escape of ammonium sulphide, together with the hydrogen sulphide.

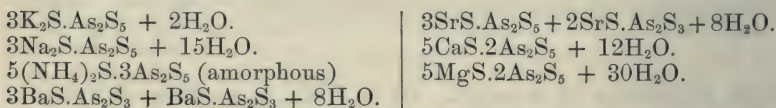
Similar acid salts are produced by treating the monobasic salts with water; thus  $K_2S.As_2S_3 + 5 \text{ aq.}$ , gives at first  $K_2S.2As_2S_3$ , and after prolonged boiling with water, the triacid salt  $K_2S.3As_2S_3$ . When the calcium salt,  $CaS.As_2S_3 + 10 \text{ aq.}$ , is treated with cold water, the brown salt,  $CaS.4As_2S_3 + 10 \text{ aq.}$ , remains behind, while warm water leaves the yellow salt,  $CaS.9As_2S_3$ .

The triacid sulpharsenites of potassium and sodium are also formed, when a boiling solution of the corresponding carbonate is mixed to saturation with arsenious sulphide. The bisulphide  $AsS_2$  is then also formed, together with well crystallised oxysulpharsenates, namely, with potassium, the previously known salt,  $K_2O.As_2S_2O_3 + 2 \text{ aq.}$ ; with sodium the salt  $Na_2O.2As_2S_3O_2 + 7 \text{ aq.}$

The saturating capacity of arsenious sulphide appears therefore to be capable of wide variation, inasmuch as salts exist containing 1, 2, 3, 4, 6, and 9 mols of  $As_2S_3$ , to 1 mol.  $R_2S$ , besides basic salts with 2, 3, 7  $R_2S$  to  $1As_2S_3$ , or  $3R_2S$  to  $2As_2S_3$ .

3. *Pentasulphide or Arsenic sulphide*,  $As_2S_5$ .—The precipitate thrown down by hydrochloric acid from a dilute solution of sodium sulpharsenate, is a sulphhydrate,  $3H_2S.As_2S_5$ , which gives up the whole of its hydrogen sulphide only after prolonged boiling.

By dissolving the pentasulphide in alkaline sulphhydrates, the following salts are obtained:—



Most of these salts are  $\frac{5}{2}$ -basic, and in some of them the pentasulphide of arsenic is partly reduced to trisulphide.

H. W.

**Crystallised Platinic Chloride.** By H. LAWROW (*Zeitschr. f. Chem.*, vii, 615).

ACCORDING to Mather, this compound contains 10 mol. of water, but according to Boedecker only 8 mol. The author finds that on evaporating an aqueous solution under the exsiccator large brown prisms are obtained, which are very deliquescent and have the composition,  $PtCl_4 + 10H_2O$ .

C. S.

**Researches on Crystalline Dissociation.** By P. A. FAVRE and C. A. VALSON (*Compt. rend.*, lxxiv, 1016—1025; and 1165—1173).

THE first of these papers contains the results of the authors' researches on the alums. From thermal experiments on various alums dissolved



in a large quantity of water (1000 equivalents), it would appear that the dissociating action of water is nearly the same for the potash and ammonia alums of chromium and aluminium, both at  $10^{\circ}$  and at  $20^{\circ}$  ( $-9499$  to  $-9889$  heat-equivalents), but much greater for ferric-potassic and ferric-ammonic alums ( $-16016$  to  $-18060$  heat-equivalents). These numbers were not found to vary sensibly even when a comparatively small proportion of water was employed to dissolve the salts. Experiments were also made with alums previously dried at  $85^{\circ}$ . The thermic results obtained may be regarded as the difference between the absorption of heat resulting from the dissociating action causing the destruction of the crystalline edifice, and the disengagement of heat proceeding from the contraction of the total volume which takes place when the salt is dissolved. Again, the 24 equivalents of water which exist in the solid state in the alums would require, if they were uncombined, 17000 heat-equivalents to pass into the liquid state, but the chromium and aluminium alums in dissolving absorb only about 9500, from which it might be inferred that the latent heat of water is considerably diminished when it is associated with the saline constituents of crystallised alums.

Aqueous solutions of the violet chrome alums, when submitted to prolonged ebullition, become green and uncrystallisable, and the addition of barium chloride to the cold solutions causes the immediate precipitation of only half the sulphuric acid they contain. The authors infer from this that the green chromium sulphate may be represented by the formula  $\text{SO}_4[\text{Cr}_2(\text{SO}_4)_2]$ , the compound  $\text{Cr}_2(\text{SO}_4)_2$  being considered as a metallic radical, *sulphochromyl*.

This was confirmed by the thermic phenomena observed on precipitating with barium chloride solutions of the chrome alums which had been altered by prolonged ebullition. Three different methods were employed. 1. An excess of barium chloride was added to the solution. 2. The theoretical quantity of barium chloride necessary to precipitate the whole of the sulphuric acid present was added half at a time. 3. The theoretical quantity of barium chloride was divided into four equal portions, which were added successively. Barium chloride precipitates, in the cold, only the sulphuric acid of the potassium or ammonium sulphate and the sulphuric acid of the sulphochromyl sulphate, forming the corresponding chlorides, whilst the sulphochromyl chloride is only slowly acted on and decomposed by the barium chloride.

The second paper contains tables of the calorific effects of dissolving aluminium sulphate in pure water, and in water containing one equivalent of potassium sulphate or ammonium sulphate, and the same salt dried at  $100^{\circ}$ ; likewise the effects produced by precipitating the aluminium sulphate with barium chloride, and the various alums with the same reagent. From the results obtained, the authors infer that the two salts of which each kind of alum is composed become dissociated on solution, and, moreover, that in the case of the ferric alums, the constituents of the ferric sulphate are also dissociated. The question then arises how the ferric oxide can remain in solution in presence of an acid which seems to have ceased to have any chemical action on it.

When a dilute solution of a ferric alum is heated, the colour gradually

becomes darker, approaching that of a cobalt salt, and on boiling the solution for a considerable length of time, ferric oxide is precipitated, united with a variable quantity of sulphuric acid. This seems to be caused by the dissociating action of heat superadded to that of the water, a view confirmed by the thermic results obtained on precipitating the alums by ammonia. The authors are of opinion that the ferric chloride formed on precipitating a solution of a ferric alum by barium chloride is in a less advanced stage of dissociation than the ferric sulphate.

C. E. G.

## Mineralogical Chemistry.

**Blegioolite, an Iron Oolite belonging to the brown Jurassic formation of the Alps, from the Glärnisch, in the Canton Glarus.** By A. BALTZER (Deut. Chem. Ges. Ber., v, 983).

THIS sedimentary rock possesses a general interest, in so far as its formation by deposition from an ancient Jura Sea admits of chemical demonstration. When the iron-ore is exhausted with water the resulting solution is found to contain the constituents of sea-water, viz., small but distinctly recognisable quantities of chlorine (bromine, iodine), magnesia, and alkalis. Specimens taken from the very middle of the compact mass contained these soluble constituents, showing that they could not have been introduced by subsequent infiltration, but must have been derived from particles of sea-water mechanically enclosed in the mass as it was deposited. The quantity of chlorine found was 0.034 p. c.

H. W.

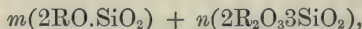
**Adamellogranite and the Mica contained in it.** By A. BALTZER (Deut. Chem. Ges. Ber., iv, 983).

THIS rock, belonging to the Adamello group (south of the Ortler), and described by vom Rath as a peculiar species, whereas Zirkel classes it with diorite, is regarded by Baltzer merely as a variety of granite.

The mica, dried at 100°, gave by analysis—

SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.
36.43	16.71	14.40	17.40	6.87	1.66	5.54	0.03 = 99.04

The oxygen ratio is RO : R<sub>2</sub>O<sub>3</sub> : SiO<sub>2</sub> = 4 : 5.88 : 9.72, whence it may be inferred that the mica is included in the general formula of the magnesia micas—



and that it exhibits the hitherto unobserved case in which  $m = 2$ ,  $n = 1$ , so that its formula is—



It is therefore a ferrous magnesia mica allied to Soltmann's lepidomelane ( $m = 1, n = 1$ ), and to Scheerer's mica from the zircon-syenite of Norway ( $m = 3, n = 1$ ).

H. W.

**Constitution of Grey Serpentine.** By STANISLAS MEUNIER  
(Compt. rend., lxxiv, 1325—1329).

SPECIMENS of serpentine from the Alps, Tuscany, Styria, Tynos, and Brazil, were greyish-green and granular, rarely schistoid in texture, and, though not sensibly magnetic, yielded to the magnet, when powdered, 0.79 per cent. of black iron oxide. They had an unctuous feel, great tenacity, and a shining or splintered and waxy fracture. Hardness = 3, sp. gr. 2.37 to 2.52. In polarized light they appeared to be mixtures of a crystalline active substance with a grey opalescent amorphous matrix, with occasional opaque grains of a metallic lustre. 98.41 per cent. of the rock was silicate attacked by hydrochloric acid, 0.80 per cent. was unattacked, and proved to be pyroxene. By the action of potash ley the rock was deprived of a portion containing nearly all the water and presenting the characters of magnesite. The residue was identified, by the microscope and by the action of hydrochloric acid, as peridot containing a small quantity of pyroxene.

C. G. S.

**Meteorite from Tjube (India).** By E. H. BAUMHAUER (Chem. Centr., 1872, 136).

THIS meteorite fell on the 9th of December, 1869. Nine hours after its fall it was still too hot to be touched by the hands. It weighed 10 kilograms and had a specific gravity of 3.496. A portion (14 p. c.) was separable by the magnet and had a specific gravity of 6.8 at 15°. The ratio of nickel to iron in the magnetic portion was 1 : 15. The siliceous portion gave by analysis—

Matter insol. in Iron	Na <sub>2</sub> O with trace								
	HCl. sulphide.	SiO <sub>2</sub> .	MgO.	FeO.	CaO.	of K <sub>2</sub> O.	Al <sub>2</sub> O <sub>3</sub> .	MnO.	NiO.
	50.14	3.71	14.95	16.40	12.01	0.74	0.32	0.22	0.30
									trace = 98.79

H. W.

**Meteoric Iron from Greenland.** By A. NORDESKIÖLD (Deut. Chem. Ges. Ber., iv. 987).

THIS iron was found by the Swedish Expedition of 1871 on the sea-shore near Disco Bay, at the foot of a basalt mountain, in three masses, weighing 300, 200, and 100 centners, together with several smaller pieces. It is very hard, crystalline, and brittle, but when moved to a warmer climate, weathers very rapidly and crumbles to a coarse-grained powder.

Metallic iron is also found in the solid basalt near the locality of the loose blocks, and on the other hand many of these loose masses are



partly encrusted with rock of the same character as the neighbouring basalt, a circumstance which seems to indicate that the loose blocks also originally belonged to the basalt. The composition of the loose and imbedded masses is likewise consistent with the supposition of a community of origin, as the following analyses will show:—

*a.* One of the larger blocks analysed by Nordenskiöld; *b.* One of the smaller loose masses analysed by Nordström; *c.* Iron from a vein in the basalt analysed by Lindström.

	<i>a.</i>	<i>b.</i>	<i>c.</i>
Iron .....	84.49	86.34	93.24
Nickel .....	2.48	1.64	1.24
Cobalt .....	0.07	0.35	0.56
Copper .....	0.27	0.19	0.19
Alumina .....	trace	0.24	—
Lime .....	—	0.48	—
Magnesia .....	0.04	0.29	trace
Potash .....	trace	0.07	0.08
Soda .....	—	0.14	0.12
Phosphorus .....	0.20	0.07	0.03
Sulphur.....	1.52	0.22	1.21
Chlorine.....	0.72	1.16	0.16
Silica.....	trace	6.66	0.59
„ undissolved.....	0.05	4.37	—
Carbon, organic matters, } oxygen, and loss ..... }	10.16	3.71	{ C 2.30 H 0.07
	<hr/> 100.00	<hr/> 105.93	<hr/> 99.79

All the three samples contain nickel. The unusually large, though varying amount of carbon is also common to them all; so likewise is the considerable proportion of chlorine, which shows itself during the weathering of the iron by the exudation of watery drops of iron chloride. The Wiedemann and Setven figures are most distinct in the iron from the basalt.

From this community of character it might perhaps be inferred that the whole consists of native metallic iron. The discoverer, however, is more inclined to regard it as due to a fall of meteorites at a very remote epoch, before the volcanic ashes had hardened into the existing basalt. The decided meteoric shape of the masses, their porosity, and the presence of organic matter,—circumstances which cannot well be reconciled with the supposition that the iron has been ejected from the interior of the earth in a state of igneous fusion,—together with the presence of nickel, &c., all afford evidence of the meteoric origin of the iron.

H. W.

### Examination and Determination of the Combined Carbon in Meteoric Iron. By JOSEPH BOUSSINGAULT (Compt. rend., lxxiv, 1287).

THE author has determined the combined carbon in some meteorites, *i.e.*, the carbon, which, as hydrocarbon, is completely removed by the

action of free acids. The iron was converted into chloride by the action of mercuric chloride. Two samples of the meteoric iron from Caille gave—

	I.	II.
Iron .....	89.53	89.73
Nickel.....	9.76	9.90
Combined carbon .....	0.12	0.12
Insoluble residue, &c. ..	0.59	0.25

Two samples of the meteoric iron from Lenarto (Hungary) contained no carbon at all.

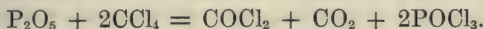
R. S.

## Organic Chemistry.

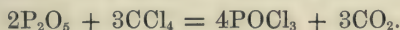
### Action of Carbon Tetrachloride on Phosphorus Pentoxide.

By G. GUSTAVSON (Zeitschr. f. Chem., vii, 615).

WHEN one mol. of phosphorus pentoxide is heated with 2—3 mol. of carbon tetrachloride to 200°—220°, the following reaction takes place:—



The quantity of phosgene produced is about  $\frac{3}{4}$  of the theoretical amount, and a portion of carbon tetrachloride remains always unchanged. By diminishing the quantity of the latter, the yield of phosgene also diminishes, while that of carbon dioxide is increased. On employing equal numbers of molecules the reaction is—



The residue in the tubes is a viscid liquid, consisting of phosphorus oxychloride and a compound formed by the action of phosphorus oxychloride on the pentoxide, which will shortly be described.

C. S.

### Oxygenated Ethyl Compounds. By E. ERLÉNMEYER (Ann. Chem. Pharm., clxii, 373—388).

(1.) FORMATION of ether from alcohol, and *vice versa*, in presence of dilute sulphuric acid, at high temperatures. The author refers to his former researches. Ether, heated in a sealed tube to 180° with 4 volumes of water and 1 c.c. dilute sulphuric acid, gave a considerable quantity of alcohol.

Alcohol heated in sealed tubes with water only gave no ether.

Alcohol heated with dilute sulphuric acid (1 : 3, 1 : 5, and 1 : 10) to 226°—230, yielded ether, ethylene, and, under certain conditions, ethylsulphuric acid.

The author concludes that—

1. Alcohol or ether heated with sulphuric acid and water at a high temperature, forms ethylsulphuric acid.

2. At a certain temperature, and with a given proportion of alcohol in the solution, ethylsulphuric acid is decomposed into sulphuric acid and alcohol.
3. At a higher temperature, or when a larger proportion of alcohol is present in the solution, ethylsulphuric acid and alcohol react so as to form ether.
4. A part of the ethylsulphuric acid is decomposed, forming ethylene and sulphuric acid, another part forming ethylene, sulphur dioxide, and water.

(2.) Formation of ether from alcohol under the influence of ethylic sulphate and ethylsulphuric acid.

Ethylic sulphate heated with the proper proportion of alcohol yields ether when distilled, and ethylsulphuric acid with *free* sulphuric acid in the residue; this residue heated to 140°, alcohol being allowed to flow on it, yields ether; the author therefore thought that the formation of ethylic sulphate might probably precede that of ether. But by experiment it was found that alcohol distilled with sulphuric acid, at a temperature at which ethylic sulphate could not form (96°), gave a large percentage of ether in the distillate, no ethylene or sulphurous acid being produced. The formation of ether at this temperature was, however, much slower than at 140°.

(3.) Gerhardt's parathionic acid.

Gerhardt prepared the barium salt of this acid, which he said was an isomeride of ethylsulphuric acid, the two barium-salts differing in their behaviour when boiled with water. The author's experiments tend to an opposite conclusion. The two barium-salts, he says, are similarly decomposed by boiling with water. They are indeed identical, and therefore ethylsulphuric and parathionic acids are one and the same.

M. M. P. M.

### Derivatives of Dichlorinated Ether. By ABELJANZ (*Deut. Chem. Ges. Ber.*, iv, 985).

THIS paper contains further communications on the oxychloroether,  $\text{CH}_2\text{OH}-\text{CHCl}.\text{O}.\text{C}_2\text{H}_5$ , obtained from dichlorinated ether and its condensation-product,  $\text{C}_8\text{H}_{16}\text{Cl}_2\text{O}_3$  (*Deut. Chem. Ges. Ber.*, iv, 624).

The author hoped that oxaldehyde would be formed by the action of concentrated sulphuric acid on oxychloroether. Sulphuric acid causes an evolution of hydrochloric acid, but when the product is agitated with ether, and the ethereal solution is neutralised with soda, filtered, and evaporated, an uncrystallisable syrup remains, having an odour of aldehyde. The analytical results obtained on treating this with silver oxide, inclined the author to believe that the oxaldehyde at first formed

is converted by the hydrochloric acid into chloraldehyde:  $\begin{array}{c} \text{CH}_2.\text{OH} \\ | \\ \text{CH.O} \end{array} +$

$\text{CH}_2\text{Cl} + \text{H}_2\text{O}$

$\text{HCl} = \begin{array}{c} | \\ \text{CH.O} \end{array}$  . The product formed by oxidation with silver oxide was found to be glycollic acid.



The condensation-product,  $C_8H_{16}Cl_2O_3$ , when treated with concentrated sulphuric acid, yields chloraldehyde, water, and ethylsulphuric acid, only a trace of hydrochloric acid being evolved.

A compound crystallising in long, rectangular, iridescent prisms, is obtained on passing ammonia through an ethereal solution of chloraldehyde, and subsequently removing the ether by evaporation. It is readily soluble in ether, and melts at  $163^\circ$ . It seems to have the  $CH_2.Cl$

formula  $\begin{array}{|c} | \\ CHCl.NH_2 \end{array}$ , or one polymeric with it.

C. E. G.

**Action of Sodium upon a Mixture of Phosgene Ether and Ethyl Iodide.** By A. GEUTHER (Jenaische Zeitschr., vii, 218—224).

SODIUM acts violently upon a mixture of phosgene ether and ethyl iodide in presence of anhydrous ether. More than half of the products formed boil between  $120^\circ$ — $130^\circ$ , and consist principally of carbonic ether mixed with compounds containing more carbon and hydrogen, the nature of which could not be ascertained. From the liquid boiling above  $130^\circ$  no definite bodies could be isolated by fractional distillation; it was, therefore, heated with an excess of strong soda-solution in sealed tubes, in a water-bath, as long as its volume diminished. The products thus formed contained carbon dioxide, ethyl alcohol, and *diethyl-acetone*,  $C_7H_{14}O$ . From this it appears highly probable that the original liquid contained *diethyl-diacetic ether* (diethylacetone-carbonic ether), which, as Frankland and Duppa have shown, yields the above products when treated with alkalis. Besides these bodies, two liquids having a higher boiling-point were isolated. That boiling at  $179^\circ$  is a colourless liquid, smelling like turpentine, and having a burning and afterwards bitter taste; it has the composition  $C_9H_{16}O_2$ . The second is a yellow oil, having a similar smell and taste, and boiling at  $249^\circ$ ; its composition is  $C_{20}H_{34}O_2$ .

C. S.

**On the Solubility of Sugar in Mixtures of Alcohol and Water of Various Strengths, and at Different Temperatures.** By C. SCHEIBLER (Deut. Chem. Ges. Ber., v, 343—350).

THE author has made careful determinations of the solubility of sugar in dilute alcohol containing 10, 20, 30, &c., per cent. of alcohol by volume. These determinations were made with solutions of sugar in the dilute alcohol, saturated at three different temperatures, namely,  $0^\circ$ ,  $14^\circ$ , and  $40^\circ$ . The tabulated results give—1. The volume-percentage of alcohol. 2. The sp. gr. of the alcoholic solution taken at a temperature of  $17.5^\circ$ . 3. The sp. gr. of an aqueous solution containing the same weight of sugar in 100 c.c. 4. The corresponding percentage of sugar according to Brix's tables (*Zeits. des Ver. f. Rübenzucker Industrie*, xv, 583, and xx, 269), and, lastly—5. The weight of sugar

contained in 100 c.c. of the solution. There are separate tables for each of the three temperatures  $0^{\circ}$ ,  $14^{\circ}$ , and  $40^{\circ}$ , but (2) is omitted in the last of these, as when cooled to  $17.5^{\circ}$  the solutions saturated at  $40^{\circ}$  deposit crystals of sugar.

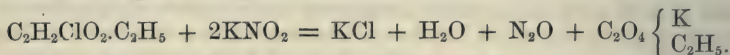
An aqueous solution of sugar saturated at  $0^{\circ}$  contains 65 per cent. sugar; at  $40^{\circ}$ ,  $75\frac{3}{4}$  per cent.; and at  $14^{\circ}$ , 66 per cent.; the latter, when mixed with an equal volume of absolute alcohol, will still remain saturated at that temperature, but the further addition of alcohol causes the separation of sugar. Sugar is but very slightly soluble in alcohol of over 90 per cent., and almost insoluble in absolute alcohol.

C. E. G.

### Action of Potassium Nitrite on Ethyl Chloracetate. By

A. STEINER (Deut. Chem. Ges. Ber., v, 383).

SCHISCHKOFF regards isocyanuric acid as the amide of nitro-acetic acid. To obtain the latter acid, an alcoholic solution of ethyl chloracetate was heated with potassium nitrite, but without success, the reaction taking place according to the equation—



Potassium ethyloxalate decomposes only above  $140^{\circ}$ , and not below  $100^{\circ}$ , as stated in handbooks.

C. S.

### Action of Potassium Permanganate on Tartaric Acid. By

A. FLEISCHER (Deut. Chem. Ges. Ber., v, 350—353).

It is well known that tartaric acid, when treated with potassium permanganate in an acid solution, yields formic acid, carbonic anhydride, and water, whilst in an alkaline solution the formic acid is also destroyed. If, however, a solution of permanganate be added to one of tartaric acid, the reaction is different; a white precipitate first makes its appearance, which, on the further addition of permanganate solution, becomes rose-red, and finally brown, from formation of manganic peroxide. If the reaction be stopped when the precipitate has become rose-coloured, it will be found that exactly half as much permanganate solution has been employed as would have sufficed for the complete decomposition of the tartaric acid in the presence of an excess of a mineral acid. The precipitate which was found to be manganese tartrate,  $\text{C}_4\text{H}_4\text{MnO}_6 \cdot 2\text{H}_2\text{O}$ , is of a deep rose-red colour, but becomes paler when dried over sulphuric acid, and almost colourless at  $100^{\circ}$ . It is scarcely soluble in cold, but somewhat more so in hot water. Nothing separates from a hot saturated solution unless sufficient alcohol be added to produce a slight turbidity, when small hard crystals are deposited on allowing it to stand for some time. This salt is readily soluble in mineral acids and in tartaric acid; the addition of alcohol to the latter solution again precipitates the neutral salt.

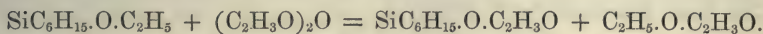
Oxalic acid, treated in the same way with potassium permanganate, yields manganese oxalate. Citric acid gives no precipitate, and the

solution leaves an uncrystallisable syrup on evaporation. No acetone is formed, as is the case when citric acid is decomposed in the presence of acids.

C. E. G.

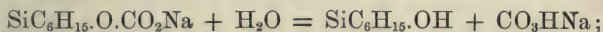
**The Silicoheptyl Series.** By A. LADENBURG (Deut. Chem. Ges. Ber., v, 319).

TRIETHYLSILICOL and acetyl chloride produce *triethylsilicol acetate*, but the product is impure as the hydrochloric acid simultaneously formed causes decomposition of the product. Triethylsilicol ether and acetic anhydride, however, readily yield the acetate after heating for a short time to  $280^{\circ}$  in a sealed tube, the reaction being—

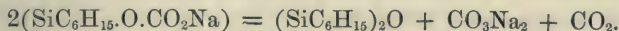


The two acetates thus produced are readily separable by distillation, triethylsilicol acetate boiling at  $168^{\circ}$ ; its vapour-density was found to be 164.7 in toluidine vapour, the formula requiring 174. Its specific gravity at  $0^{\circ}$  is 0.9039. Moisture slightly decomposes it, but to produce perfect decomposition long-continued boiling with sodium carbonate is required; this is a convenient method of preparing pure triethylsilicol.

Triethylsilicol gives a compound with sodium, hydrogen being evolved; on passing dry carbon dioxide into the ethereal solution of this compound, a precipitate is produced consisting of the salt  $\text{SiC}_6\text{H}_{15}.\text{O}.\text{CO}_2\text{Na}$ ; this body is very easily decomposed by moisture, in accordance with the reaction—

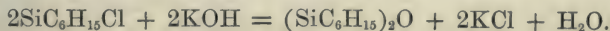


and by heat, with production of silicoheptyl oxide and sodium carbonate, thus—

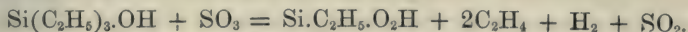


This is the first compound containing silicon, carbon, and sodium which does not yield sodium silicate, but does form sodium carbonate on ignition.

Phosphoric anhydride readily attacks triethylsilicol, with formation of a body which has the composition of the *silicoheptyl oxide* of Friedel and Crafts, and also the same boiling-point; it has, however, no unpleasant smell, in spite of which the author believes in the identity of the two bodies; the same compound, destitute of smell, is obtained by the action of caustic alkalis on silicoheptyl chloride—



also apparently by dissolving triethylsilicol in concentrated sulphuric acid, and diluting the solution. Fuming sulphuric acid gives rise to a different reaction, viz. :—





*silicopropionic acid* being formed: hence it appears that *triethylsilicol* behaves just as a *tertiary alcohol*; chromic acid and potassium permanganate have no action on it.

Bromine added to triethylsilicol drop by drop gives rise to hydrobromic acid, and a brominated body not decomposed by water or by potassium acetate, at 120°, but readily yielding up its bromine on warming with alcoholic potash.

Silicoheptyl ether is attacked by zinc-ethyl and sodium, but apparently silicon ethyl is not produced, though the formation of this body might have been expected. These last products are undergoing further investigation.

C. R. A. W.

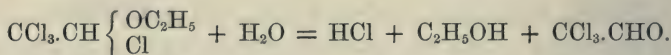
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**On the Formation of Chloral.** By A. WURTZ and G. VOGT  
(Compt. rend., lxxiv, 777—784).

WHEN aldehyde is acted upon by chlorine, the group CHO is attacked, and acetyl chloride results. But when the group CHO in aldehyde is replaced by  $\text{CHCl}(\text{OC}_2\text{H}_5)$ , as in the compound formed by Wurtz and Frapoli, by passing a current of hydrochloric acid gas into a mixture of alcohol and aldehyde, the action of chlorine in presence of iodine gives rise to  $\text{CCl}_3\text{CH} \begin{Bmatrix} \text{OC}_2\text{H}_5 \\ \text{Cl} \end{Bmatrix}$ .

This body is identical with the tetrachlorinated ether of Malaguti, and with the compound recently described by Henry as the product of the action of phosphorus pentachloride on chloral alcoholate.

This tetrachlorinated ether is readily converted into chloral by heating with water:

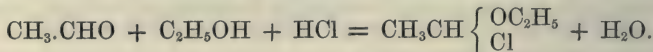


When heated with alcohol instead of water, it yields hydrochloric acid and trichloroacetal,  $\text{CCl}_3\text{CH} \begin{Bmatrix} \text{OC}_2\text{H}_5 \\ \text{OC}_2\text{H}_5 \end{Bmatrix}$ .

The latter, by the action of sulphuric acid, yields chloral.

The tetrachlorinated ether also gives ethyl chloride and chloral when distilled with sulphuric acid.

The authors consider that it is by this succession of changes that chloral is formed in the ordinary process for its manufacture, namely, by passing chlorine into alcohol. The water necessary for the decomposition of the tetrachlorinated ether results, independently of that which may be present in the alcohol, from the action of the hydrochloric acid generated, upon the alcohol and aldehyde:



Monochlorinated ether of  
Wurtz and Frapoli.

As to the source of the aldehyde, Stas has already shown that it is a product of the action of chlorine upon alcohol, although obviously it

can never accumulate to any extent, inasmuch as it is at once attacked by the alcohol and hydrochloric acid.

Theoretically it should be possible to substitute water for alcohol in the process described by the authors. Under such circumstances the formation of the body  $\text{CH}_3\text{CH} \begin{Bmatrix} \text{OH} \\ \text{Cl} \end{Bmatrix}$  is conceivable.

This compound corresponds to the monochlorinated ether of Wurtz and Frapolli, and may be regarded as the chlorhydrin of ethyldene glycol,  $\text{CH}_3\text{CH} \begin{Bmatrix} \text{OH} \\ \text{OH} \end{Bmatrix}$ .

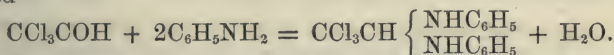
The action of chlorine on such a body should yield chloral.

Adopting this idea the authors have succeeded in establishing the fact that chloral is really formed in notable quantity when chlorine is passed into a cooled mixture of aldehyde and aqueous hydrochloric acid, or even of aldehyde and water.

W. A. T.

#### Action of some Amido-compounds on Chloral. By O. WALLACH (Deut. Chem. Ges. Ber., v, 251—257).

By the action of aniline on chloral, a crystalline body, trichlorethylidene-diphenylamine, corresponding to Schiff's ethyldene-diphenylamine, is obtained—



It melts at  $100^\circ$ — $101^\circ$ , but soon decomposes when kept at this temperature. It is insoluble in water and decomposed when boiled with water or alcohol, evolving a penetrating odour like that of phenyl cyanide. Treated with acids it undergoes decomposition, yielding salts of aniline. The compound therefore appears not to possess the basic properties ascribed to it by the author in a former communication.

Hydrochloric acid gas passed into its solution in benzene causes the formation of a large quantity of aniline hydrochloride, and an oily body which has not as yet been obtained in a state fit for analysis.

Toluidine acts upon chloral in the same manner as aniline, giving rise to trichlorethylidene-ditolylamine,  $\text{CCl}_3\text{CH} \begin{Bmatrix} \text{NHC}_6\text{H}_4\text{CH}_3 \\ \text{NHC}_6\text{H}_4\text{CH}_3 \end{Bmatrix}$ , a crystalline body which melts at  $114^\circ$ — $115^\circ$ .

When alcohol is added to the crude product of the reaction before cooling, large crystals of the compound  $\text{CCl}_3\text{CH} \begin{Bmatrix} \text{OC}_2\text{H}_5 \\ \text{NHC}_6\text{H}_4\text{CH}_3 \end{Bmatrix}$  are obtained, melting at  $76^\circ$ — $77^\circ$ .

Compounds of chloral with acetamide and with benzamide have been also studied by the author. Acetamide-chloral,  $\text{CCl}_3\text{COH} \cdot \text{CH}_3\text{CONH}_2$ , melts at  $156^\circ$ — $157^\circ$ , and when distilled, yields first chloral, afterwards acetamide, leaving a black residue. With aqueous alkalis it gives chloroform, and with dilute acids in the presence of alcohol furnishes ethylic acetate.

Benzamide chloral melts at  $150^\circ$ — $151^\circ$ .

The author is studying the action of potassium cyanide upon chloral, with the view of replacing the three chlorine-atoms by cyanogen.

W. A. T.

**Note on Dichlorhydrin.** By A. WATT (Deut. Chem. Ges. Ber., v, 257—259).

ACCORDING to Hübner and Müller, the dichlorhydrin formed by Berthelot's process, by passing hydrochloric acid gas into a mixture of glycerin and glacial acetic acid, is a mixture of two isomeric bodies. Watt has repeated the experiment of distilling the product in fractions, and finds that the greater part passes over between  $173^{\circ}$  and  $175^{\circ}$ , and that the portion, the boiling point of which lies between  $182^{\circ}$  and  $184^{\circ}$ , is not homogeneous, as stated by Hübner and Müller, but is resolvable into two portions of lower and higher boiling point respectively. The latter is very small in quantity, and he therefore concludes that a second dichlorhydrin is not produced, at least in notable proportion.

The dichlorhydrin the author has examined has a specific gravity 1.369 at  $16^{\circ}$  and boiling point  $176^{\circ}$ — $177^{\circ}$ . By oxidation with chromic acid it gave an acid which appeared to be monochloracetic acid and a small quantity of dichloracetone. Oxidized by nitric acid, it gave oxalic acid and a small quantity of an oil possessing the smell of chloropicrin.

W. A. T.

**On Chloral Sulphydrate.** By H. BYASSON (Compt. rend., lxxiv, 1290—1792).

ANHYDROUS chloral readily absorbs sulphuretted hydrogen, and after the action of the gas has been continued for about twenty-four hours, the whole solidifies to a white crystalline mass, which may be purified by distillation and subsequent crystallisation from ether or from absolute alcohol. Chloral sulphydrate,  $C_2HCl_3O.H_2S$ , crystallises in rhomboidal plates or quadrangular prisms, which have a disagreeable odour and characteristic taste, recalling that of chloral hydrate. It melts at  $77^{\circ}$  and boils at  $123^{\circ}$ . It is soluble in all proportions in anhydrous alcohol, ether, or chloroform, but is decomposed by water, with deposition of sulphur, the action being very complex. Alkaline solutions yield chloroform and an alkaline formate and sulphydrate. Nitric acid oxidizes it with formation of trichloracetic acid. Sulphuric acid has no action in the cold, but when heated with it gives rise to anhydrous chloral, whilst sulphuretted hydrogen and sulphurous anhydride are evolved and sulphur is deposited.

The physiological action of chloral sulphydrate is very similar to that of chloral hydrate, causing sleep and a slight acceleration of the movements of the heart, as was shown by administering .20 to .30 grm. of the compound to guinea-pigs by subcutaneous injection of the ethereal solution.

C. E. G.

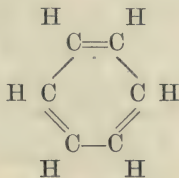
**On some Condensation-products of Aldehyde.** By AUG. KEKULÉ (Ann. Chem. Pharm. clxii, 77—124 and 309—320).

I. *Theoretical Considerations and Historical Notes on the Constitution of Benzene.*\*—Although the hypothesis as to the mode of union of the

\* Much of the matter contained in the earlier portion of this paper is fully discussed in the Supplementary volume to Watts's Dictionary of Chemistry, Art. Aromatic Series, and is therefore not reproduced here.—H. E. A.



carbon atoms in benzene brought forward by Prof. Kekulé in his memoir on the constitution of the compounds of the aromatic series has in general been tacitly accepted; nevertheless, it has often been the subject of discussion, and numerous modifications have been proposed. It will be remembered that the author's original hypothesis was that the six atoms of carbon may be regarded as united by one and two affinities of each alternately, so as to form a ring-like closed chain, as represented by the symbol—



and he is still inclined to regard this view as more in accordance with observed facts than either of those since proposed, the relative values of several of which are discussed in the present memoir. It is more especially in explaining the formation of additive compounds from benzene, however, that the hypothesis in question has the advantage over all others,\* and it is on this account chiefly that the author has been led finally to give it the preference.

Two objections have been raised against Kekulé's benzene formula:

1. That, since according to it, the six atoms of hydrogen in benzene are of equal value,† only one pentachlorobenzene is possible, whereas two are said to exist. The author considers, however, that too great weight is not to be attached to this objection, the experimental demonstration of the existence of two such compounds being still incomplete.

The second objection, which at first sight appears of more importance, is the following:—It is argued that those bi-derivatives, in which the substituting radicles occupy contiguous positions, should differ according as the replacement has taken place on adjacent carbon atoms united by one affinity (C—C), or by two affinities (C=C); the so-called 1 : 2 derivatives should therefore be isomeric with the 1 : 6 derivatives, so that 4 bi-derivatives of benzene are possible, whereas hitherto at most 3 have been obtained. Many consider that the difference in such a case would be so slight as to be unrecognisable. The author believes that this view takes its origin rather from the model employed than from the ideas of which this model affords a somewhat imperfect representation, and to show that in his opinion no such difference exists, he brings forward the following hypothesis as to the mode of motion of the atoms in the benzene molecule.

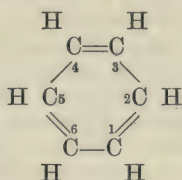
The atoms in the systems which we term molecules must be considered as in continuous movement; no explanation, however, has hitherto been given as to the nature of the intramolecular motion. A planetary motion appears inadmissible in face of the law of the linking

\* See Watts's *Dictionary*, *loc. cit.*

† This has been experimentally demonstrated. (Huebner, *Ann. Chem. Pharm.*, clvi, 308.)

of atoms (*Verkettung*) now recognised in chemistry. The motion must indeed be of such a nature that all the atoms of the system retain the same relative arrangement, or in other words, that all the atoms return to a mean position of equilibrium. The most probable assumption then appears to be that the separate atoms of the system, possessing an essentially rectilinear motion, strike one against the other and, being elastic bodies, then recoil. What in chemical language is termed equivalency (atomicity) acquires therefore a more mechanical signification: the equivalency is the relative number of contacts which occur in the unit of time between the atoms. In the same time that the univalent atoms of a monatomic molecule strike against each other once, the bivalent atoms of a diatomic molecule come twice in contact at the same temperature. In a molecule consisting of two univalent and one bivalent atoms the number of contacts in the unit of time is equal to two in the case of the bivalent atom, equal to one in the case of each monovalent atom. When, as we now express it, two atoms of carbon are united by one affinity of each, they strike against each other once in the unit of time, that is to say, in the time during which the univalent hydrogen makes one complete vibration; during the same unit of time they also each encounter three other (univalent) atoms. Carbon atoms which we consider to be united by two affinities of each strike against each other twice, and during the same time only twice come in contact with other atoms.

Applying this view to benzene, the formula proposed by the author is an expression of the following conception:—Each carbon atom strikes against two other carbon atoms during the unit of time, once against the one and twice against the other. In the same unit of time it also comes once in contact with the hydrogen atom, which during the same period makes one complete vibration. Representing benzene by the well-known hexagon formula, and having regard to any one of the six atoms of carbon, that denoted by 1 for example—



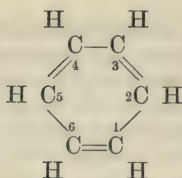
the contacts of this atom during the first unit of time may be thus represented—

1.                    2, 6, h, 2,

in which h denotes hydrogen. The vibrations of the same atom during the second unit of time are then as follows—

2.                    6, 2, h, 6.

Whereas the contacts during the first period are represented by the above formula, those occurring during the second unit of time are represented by the following—



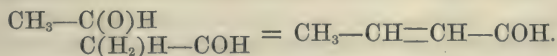
The same carbon-atom is therefore, during the first unit of time, united, as we say, by two affinities to one of the contiguous carbon-atoms; during the second, by two affinities with the other contiguous atom.

The number of contacts made by the carbon-atom during the first two units of time—the vibrations completed during these intervals are periodically repeated—are then as follows—

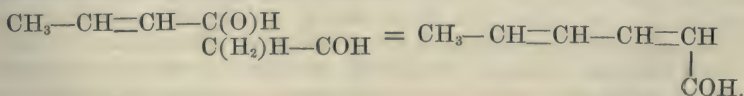
2, 6, h, 2, 6, 2, h, 6,

from which it is evident that each carbon-atom strikes against each of the two carbon atoms upon which it impinges an equal number of times, or, in other words, that it bears the same relation to both contiguous atoms. The ordinary benzene formula only represents the contacts made during the first unit of time, and thus it is that the false view has sprung up that bi-derivatives in which the radicles occupy the positions 1 : 2 and 1 : 6 respectively must be different. If the above, or some similar conception be correct, it follows that no real difference exists.

II. *Condensation of Aldehyde with separation of Water.*—Believing the question as to the internal constitution of benzene to be capable of direct proof, the author has investigated the condensation-products of aldehyde. Lieben (*Ann. Chem. Pharm.*, cvi, 336) had already found that under the influence of certain salts aldehyde was converted into a product to which he gave the formula,  $\left. \begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix} \right\} O$ , regarding it as the ether of aldehyde; and Baeyer (*Ann. Chem. Pharm.* sup., v, 79) by acting with hydrochloric acid, and treating the product with phosphorus pentachloride, obtained, among others, a chlorinated compound, which he regarded as derived from  $C_6H_{10}O_2$ , formed by the condensation of three molecules of aldehyde with separation of one molecule of water. The author was inclined from the commencement to regard it as most probable that in the first place condensation would occur between two molecules with separation of one molecule of water, according to the following equation, in which the atoms removed on condensation are bracketed—



and that condensation between this product and a third molecule of aldehyde would then take place as follows—





By removing the elements of water from this product, or two molecules of hydrochloric acid from the corresponding chloride,  $C_6H_8Cl_2$ , either benzene or a hydrocarbon of the same composition would probably be obtained. The formation of benzene, if not absolute proof of the correctness of the formula proposed by the author, would at least render it very probable. Experiment has shown that condensation does occur as premised by the author, but the second product ( $C_6H_8O$ ) is obtained with such difficulty that it has hitherto been impossible to produce either benzene or any hydrocarbon of that composition from it.

As products of the action of hydrochloric acid on aldehyde, the compounds  $C_4H_6O$ ,  $C_4H_7ClO$ , and  $C_{10}H_{18}Cl_2O_3$  have been obtained. The first proves to be identical with Bauer's acraldehyde (*Ann. Chem. Pharm.*, cvi, 336), obtained by the action of zinc chloride on aldehyde, to which the formula  $C_4H_8O_2$  was formerly assigned, and with Lieben's aldehyde ether; in the pure state it is a substance of considerable stability, and only exhibits the great tendency to change noticed by Baeyer and Lieben when it contains traces of hydrochloric acid or other impurities; on oxidation—even by exposure to the air—it is readily converted into crystalline crotonic acid. The first condensation-product of aldehyde is therefore *crotonic aldehyde*, which, it can scarcely be doubted, is formed in the manner expressed in the above equation. Traces of hydrochloric or sulphuric acid, of zinc chloride, of the salts employed by Lieben, and of many other salts, were found to exert the same condensing action on aldehyde.

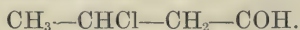
*Crotonic Aldehyde*,  $C_4H_6O$ .—The best yield is obtained by the following method:—Pure aldehyde is heated in soda-water bottles with very little zinc chloride and a few drops of water for a day or two at  $100^\circ$ . The unchanged aldehyde is then distilled off, and the distillation continued in a current of steam; the residue contains higher condensation-products. The crotonic aldehyde distils over with the steam and partly floats on the water in the receiver, partly dissolves in it; by redistilling the solution, collecting the first portion apart, the greater part may, however, be recovered.

Crotonic aldehyde boils at  $104^\circ$ — $105^\circ$ ; it is a colourless liquid, the odour of which, at first pleasant and fruity, afterwards becomes very penetrating, like that of acrolein; it is moderately soluble in water.

*Crotonylene Chloride*,  $C_4H_6Cl_2$ , obtained by acting on the aldehyde with  $PCl_5$ , is a colourless liquid boiling at  $125^\circ$ — $127^\circ$ , which is decomposed by alcoholic potash. By this latter reaction the author had hoped to obtain first,  $C_4H_5Cl$ , and afterwards the hydrocarbon,  $C_4H_4$  (diacetylene), but has not yet obtained either in a state of purity, a portion only of the chloride undergoing decomposition, and that with simultaneous formation of resinous products.

*Chlorobutyric Aldehyde*,  $C_4H_7ClO$ , is a crystalline compound obtained by the direct union of crotonic aldehyde and hydrochloric acid. The same body was present, as above stated, among the products of the direct action of hydrochloric acid on aldehyde. It melts at  $96^\circ$ — $97^\circ$ , and is insoluble in water. It has not yet been converted by oxidation into chlorobutyric acid; in one experiment, together with traces of a

chlorinated acid, much acetic acid was formed, which renders the following formula probable:—



Heating with sulphuric acid regenerates crotonic aldehyde. On boiling with silver oxide and water it gave a crystalline salt of the composition of silver oxybutyrate.

*Chlorinated Compound*,  $\text{C}_{10}\text{H}_{18}\text{Cl}_2\text{O}_3$ .—The formation of this body—a crystalline substance melting at  $98^\circ$ —by the action of hydrochloric acid on aldehyde is described at length. Very small quantities only are obtained, and the author can give no opinion as to the nature of the substance.

*Higher Condensation-products*.—Both from the portion of higher boiling-point remaining after distilling off the crotonic aldehyde, and from a product obtained by heating crotonic aldehyde with twice its weight of aldehyde and some zinc chloride for 96 hours to  $100^\circ$ , an oily product was isolated, boiling at about  $172^\circ$ , analysis of which gave numbers corresponding to the formula  $\text{C}_6\text{H}_8\text{O}$ . On exposing small quantities of this oil to the air, crystalline needles were formed, and on boiling it with water and silver oxide, a crystalline, difficultly soluble silver salt was produced, containing an amount of silver closely corresponding with the formula  $\text{C}_6\text{H}_7\text{AgO}_2$ . This was probably the triple condensation-product of aldehyde; small quantities only were obtained, however, and all attempts to convert it into benzene by the withdrawal of the elements of water were unsuccessful. On rectification of the products of still higher boiling-point an oil was separated, possessing nearly the composition  $\text{C}_8\text{H}_{10}\text{O}$ .

With regard to the mode of action of zinc chloride, and of the numerous other salts which have the above-described condensing action on aldehyde, our present knowledge warrants the assumption that in an aqueous solution of zinc chloride, together with the hydrated molecules, there are a certain number of anhydrous molecules always present; these are always in motion, and constantly change their condition, the hydrated molecules becoming anhydrous, the anhydrous molecules becoming hydrated, in such a way, however, that a mean condition of equilibrium is always preserved. If then bodies are present from which the elements of water can be withdrawn, a certain, although probably small, proportion of those molecules which are in the act of taking up water cause the separation of water from these substances, and combine with the water thus separated, so that in course of time a very small quantity of such an agent is capable of performing a large amount of work. It is evident that heat is not absolutely necessary for the production of such reactions, although an increase of temperature has an accelerating influence. In fact the author finds that aldehyde, mixed with zinc chloride, undergoes the same change in a few weeks at summer temperature, in some months at autumn and winter temperatures, as when heated for several hours to  $100^\circ$ . The action of zinc chloride and similar salts might also be referred to the presence of hydrochloric acid, for it will be generally admitted that an aqueous solution of the former always contains free hydrochloric acid and free zinc oxide.

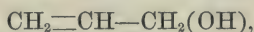
Similar considerations apply to the decomposition of complex compounds with assumption of the elements of water. Thus that of the glucosides in presence of traces of sulphuric acid may probably be referred to an action of the same nature.

The author points out that such reactions as the above indubitably play a most important part in plant life: for we know that salts which exert an action similar to that of zinc chloride are present in all parts of the plant, and the experience gained with aldehyde shows that condensation is produced by minimum quantities, even in the presence of water, and at ordinary temperatures. The various phases of chemical activity in the plant are then discussed.

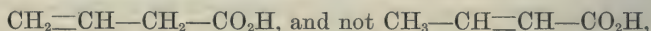
*Crotonic Acid*,  $C_4H_6O_2$ , obtained by oxidation of crotonic aldehyde, either by free oxygen or by silver oxide, crystallises in monoclinic prisms; it melts at  $72^\circ$ , and boils at  $184.7^\circ$  (corrected). On fusion with potash it yields acetic acid as sole product, each molecule of crotonic acid giving two molecules of acetic acid. Since from the mode of formation of crotonic aldehyde from aldehyde it can scarcely be doubted that in it the two middle carbon-atoms are united by two affinities of each, the author regards the production of acetic acid as an experimental demonstration of the law proposed by various chemists, that in the acids of the acrylic series the splitting up on fusion with potash always occurs between the carbon atoms which are doubly united.

The objections raised against the author's formula for crotonic acid are next discussed.

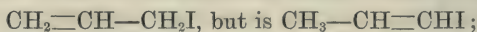
It is argued that since allyl alcohol has been proved to possess the constitution—



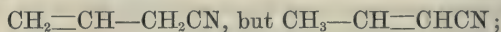
the crotonic acid from aldehyde must be—



as assumed by the author, since it is identical with the acid from allyl cyanide prepared from allyl alcohol. Regarding the correctness both of his own formula for crotonic acid, and that assigned to allyl alcohol, as established, the author is inclined to believe that, at some stage of the conversion of the alcohol into crotonic acid, a change occurs: either that the iodide prepared from the alcohol has no longer the formula—



or that the cyanide is not—



or that the cyanide constituted according to the first formula yields an acid corresponding to the second cyanide. Experiments which promise to throw light on the question are at present being carried out.

IV. *Condensation of Aldehyde, with Assumption of Hydrogen.*—The conversion of aldehyde into butylene glycol described under the above heading, has already been noticed in this Journal (x, 397).



Of extreme interest are the author's remarks on oxidation with chromic and nitric acids, which he regards as a method equally applicable to the determination of the constitution of compounds such as the acids of the acrylic series, for example, as the older method of fusion with potash. In each case a division of the molecule between the carbon atoms which are united by two affinities of each is caused.

Thus, on fusion of crotonic acid with potash, a division of the molecule occurs between the carbon atoms which are doubly united,  $\text{CH}_3\text{—CH=CH—CO}_2\text{H}$ ; the one-half of the molecule then takes up oxygen, or, more strictly speaking, the group  $\text{O}_2\text{K}$ , whilst the other half unites with hydrogen, thus forming a second molecule of acetic acid.

On oxidation of crotonic aldehyde,  $\text{CH}_3\text{—CH=CH—CHO}$ , the same splitting apart of the doubly united carbon atoms occurs; the one-half of the molecule combines with oxygen, forming acetic aldehyde, which then undergoes further oxidation; the other half yields in the first instance an aldehyde of oxalic acid, which in its turn is converted into oxalic acid. If chromic acid be the oxidiser employed, the oxalic acid also undergoes decomposition; with nitric acid the greater portion remains unaltered.

H. F. A.

**On the Constitution of Benzene.** By A. LADENBURG (Deut. Chem. Ges. Ber., v, 322).

THE author refers to the researches of Hübner and Petermann, and of Carstanjen, from which he draws the conclusion that each carbon atom in benzene corresponds to two pairs of equivalent hydrogen atoms; the ordinary benzene formula of Kekulé not sufficing for this condition, some positive evidence is obtained in behalf of the formula denoted by the author as the *second benzene hypothesis of Kekulé*.

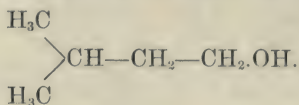
Kekulé having recently endeavoured to bring all known facts into harmony with his benzene scheme, by laying down a mechanical exposition of the mutual connections of the atoms (see the last paper), the author briefly discusses the consequences of this proposition, distinguishing the two separate points—(1) the nature of the notion of equivalence, and (2) the acceptance of one of two positions of unstable equilibrium of an atom in a molecule.

C. R. A. W.

**Products of Oxidation of Aromatic Hydrocarbons.** By A. POPOFF and TH. ZINCKE (Deut. Chem. Ges. Ber., v, 384—386).

By oxidising amyl-benzene with potassium dichromate and dilute sulphuric acid, the only products formed are benzoic acid and *isobutyric acid*. From this it appears that the study of the products of oxidation of aromatic hydrocarbons offers not only a means for determining the constitution of these hydrocarbons, but also of that of the alcohol-radicles linked to the aromatic nucleus, the formation of isobutyric

acid being a further proof that amyl alcohol has the following constitution:—



C. S.

**Action of Alkalis on Nitrobenzene.** By MERZ and CORAY  
(Deut. Chem. Ges. Ber., iv, 981).

A POWERFUL reaction takes place on heating nitrobenzene with potassium hydrate, so that it is advisable to moderate its violence by diluting the former with aniline; ammonia is given off, and on pouring the product into dilute hydrochloric acid, a brown tarry residue is left undissolved, which after a time solidifies to a crystalline mass of azobenzene. This may be purified by crystallisation from a mixture of alcohol and ether, after the resinous matter has been removed by distillation in a current of steam, or by treating it with a solution of caustic soda. The mother-liquor from which the azobenzene has crystallised appears to contain azoxybenzene. As ammonia was evolved in this reaction, it was to be expected that aniline was formed at the same time. This was found to be the case, one portion of the nitrobenzene being destroyed, and acting as a reducing agent on another portion in the presence of the potassium hydrate. Aniline, azobenzene, and ammonia, however, are only the end-products, for if the reaction be stopped at a certain stage the mass dissolves almost completely in water, and hydrochloric acid precipitates from the solution dark flocks of a resinous acid. Nitrotoluene gives toluidine and ammonia when heated with potassium hydrate, but no azobenzene. The higher nitro-compounds, such as dinitrobenzene and dinitronaphthalene, are charred under these circumstances. Sodium hydrate acts in the same manner as potassium hydrate, but less violently.

C. E. G.

**Notes on the Phenols.** By L. DUSART and CH. BARDY (Compt. rend., lxxiv, 1052—1053).

THE following facts demonstrate a close analogy in properties between phenols and the alcohols proper.

Phenyl chloride, produced by the action of chlorine on benzene, or of hydric or phosphoric chloride on phenol, is decomposed at 300° by aqueous soda, with reproduction of phenol. Chlorinated toluene, and naphthyl bromide, by the same treatment yield respectively hydrate of cresyl and naphthol.

Equal weights of sodium sulphophenate, water, and barium chloride, heated to 240° for four hours, generate free phenol in theoretical quantity. Sulphophenic acid, heated to 225° with its own weight of alcohol, gives the phenetol of Cahours.

With regard to the late announcement of the authors that phenol, heated to 250° with hydrochloric acid and aniline hydrochloride, gives

diphenylamine, MM. Girard and De Laire, finding that aniline hydrochloride heated alone to  $300^{\circ}$  furnishes the same product, have denied to phenol any part in its formation. In presence, however, of hydrochloric acid, the aniline salt is stable at  $260^{\circ}$ , whereas if phenol be added the decomposition begins at  $215^{\circ}$ . The authors attribute the reaction to phenyl chloride in the *nascent state*; hence a mixture of already formed phenyl chloride with ammonium chloride fails to yield the result.

C. G. S.

**Synthesis of Orcin.** By G. VOGT and A. HENNINGER (Compt. rend., lxxiv, 1107—1109).

ON heating chlorotoluene,  $C_6H_4Cl.CH_3$ , to  $100^{\circ}$  for some hours with sulphuric acid, two isomeric chlorocresylsulphurous acids,  $C_7H_6Cl.SO_3H$ , are produced, which may be separated by the fractional crystallisation of their barium salts. The less soluble salt, barium  $\alpha$ -chlorocresylsulphite,  $(C_7H_6ClSO_3)_2Ba + 2H_2O$ , forms beautiful colourless rhombic plates, whilst the other, viz.: barium  $\beta$ -chlorocresylsulphite  $(C_7H_6ClSO_3)_2Ba + 1\frac{1}{2}H_2O$ , which is much more soluble, crystallises in mamellated tufts, consisting of small crystalline grains. The potassium  $\alpha$ -chlorocresylsulphite, obtained by double decomposition from the corresponding barium salt, forms nacreous plates, moderately soluble both in cold water and in boiling alcohol. When this is fused with twice its weight of potassium hydrate, it becomes brown, and disengages hydrogen, while orcin, salicylic acid, and cresol are produced. The aqueous solution of the fused mass is agitated, first with benzene to remove the salicylic acid and cresol, then with ether, which dissolves the orcin and leaves it in an impure state on evaporation. After being purified, this orcin was found to be identical both in its properties and crystalline form with that prepared from the lichens, thus showing it to be a toluenediphenol,  $C_7H_6.HO.HO$ .

Orcin is the principal product of this reaction, the cresol and salicylic acid formed at the same time resulting from the action of the potassium hydrate on the potassium cresylsulphite; the latter is produced from the potassium chlorocresylsulphite by the reducing action of the hydrogen formed during the fusion.

C. E. G.

**Artificial Alizarin.** By F. REVERDIN (Deut. Chem. Ges. Ber., iv, 978).

ON submitting artificial alizarin to sublimation, and then treating the product with soda-solution, bright yellow needles are left undissolved, which, although too small in quantity for analysis, were proved not to be anthraquinone. In order to separate the monoxanthraquinone which generally accompanies artificial alizarin, it is better to treat it with milk of lime than with baryta-water, as barium alizarate is slightly soluble in water. When distilled, both barium and calcium alizarate give anthraquinone, which sublimes in bright yellow needles entirely



free from tarry matter. The corresponding purpurin compounds yield a brown oil which solidifies after a time.

The crude alizarin was found to yield finer tints than the sublimed.  
C. E. G.

**Artificial Alizarin.** By G. AUERBACH (Deut. Chem. Ges. Ber., iv, 979).

IN order to prepare pure alizarin from the crude artificial product, the author dissolves it in caustic soda, and passes a current of carbonic anhydride through the solution. A red precipitate is thus formed, consisting of sodium bicarbonate, alizarin, and sodium alizarate, and at the same time orange-coloured crusts of alizarin are deposited on the sides of the vessel. After washing the precipitate, and decomposing it with an acid, the alizarin is obtained in fine orange-coloured flocks, which dissolve completely in a solution of caustic soda with a blue tint.

C. E. G.

**Notice on Benzene Derivatives.** By IRA REMSEN (Deut. Chem. Ges. Ber., v, 379).

PURE terephthalic acid is obtained by treating parasulphobenzoic acid by Merz's method.

Paratoluenesulphamide oxidized by potassium dichromate and sulphuric acid, gives an acid still containing the group  $\text{SO}_2\text{NH}_2$ , its formula being  $\text{C}_6\text{H}_4 \begin{cases} \text{SO}_2\text{NH}_2 \\ \text{CO.OH} \end{cases}$ .

Negative results only were obtained in an attempt to convert phenol-metasulphonate of potassium (from which pyrocatechin is obtainable) into isophthalic acid by treatment with phosphoric pentachloride, treatment of the product with water and lead hydrate, so as to get the lead salt of metachlorobenzene-sulphonic acid, conversion of this into potassium salt, distillation with potassium cyanide, and treatment with alcoholic potash.

C. R. A. W.

**On the Iodized Products of the Isomeric Acids,  $\text{C}_7\text{H}_6\text{O}_3$ .** By HLASIWETZ and WESELSKY (Deut. Chem. Ges. Ber., v, 380).

SALICYLIC, oxybenzoic, and paraoxybenzoic acids do not give the same results on treatment with iodine in presence of mercuric oxide; and the study of the products obtained appears likely to throw some light on the isomerism of the benzene derivatives.

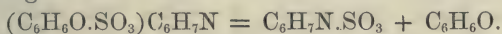
C. R. A. W.

**Paraphenolsulphonic Acid.** By E. KOPP (Deut. Chem. Ges. Ber., iv, 977—978).

PHENOL, when heated to  $80^\circ$  or  $100^\circ$  with an equal quantity of sulphuric acid for 36 hours, is converted almost entirely into paraphenolsulphonic

acid, crystallising in colourless, glistening needles, which readily deliquesce. The author, in conjunction with Follenius, has examined several salts of this acid, and studied the action of oxidising agents on them.

*Aqua regia* gives with the calcium salt a crystalline yellow compound, which dyes wool readily, and the addition of hydrochloric acid to the mother-liquor (?) produces a white crystalline precipitate. The zinc salt, when oxidised, yields a brown oil which forms, with alkalis, readily crystallisable detonating salts. Free paraphenolsulphonic acid gives, with potassium chlorate, a yellow body crystallising in small needles; with potassium chlorate and nitric acid a brown oil similar to that obtained by the oxidation of the zinc salt, and at the same time a yellow substance crystallising in small needles; potassium chlorate and hydrochloric acid gives a brown crystalline mass. Prof. Tuschschmid has obtained nitrophenolsulphonic acid by nitrating paraphenolsulphonic acid in alcoholic solution. The oxidation of the mercury salt by means of arsenic acid, gives a yellow crystalline compound. Aniline paraphenolsulphate crystallises in colourless plates, which are readily soluble in hot water, moderately so in the cold; they melt at  $170^{\circ}$ , and begin to decompose at  $190^{\circ}$ , sulphanilic acid being formed, and nearly pure phenol distilling over:



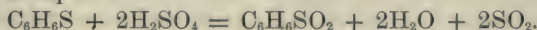
Aniline metaphenolsulphate resembles the above in its crystalline form, and decomposes in a similar manner when heated, the sulphanilic acid produced being identical with that from the para salt.

C. E. G.

**Benzene-disulphonic Acid.** By WISLICENUS and BRUNNER  
(Deut. Chem. Ges. Ber., iv, 984).

THIS acid was prepared by the action of sulphuric anhydride on benzene-monosulphonic acid. Its potassium salt mixed with potassium cyanide and subjected to dry distillation yielded, together with a large quantity of ammonia, a liquid consisting of benzene, benzonitrile, and a body which did not boil at  $195^{\circ}$ , and solidified on cooling. This substance is paradicyanobenene (1 : 4), for when boiled with an alkali it yields terephthalic acid. Benzene-disulphonic acid prepared in the ordinary way is therefore, for the most part, a para-compound.

With the view of obtaining an isomeric benzene-disulphonic acid, an attempt was made to convert thiophenol by means of sulphuric acid into thiophenol-sulphonic acid, which might be afterwards converted by oxidation into a benzene-disulphonic acid; but the expected reaction did not take place. Thiophenol dissolves in sulphuric acid at ordinary temperatures, forming a splendid blue liquid (regarded by Kolbe as tolylic sulphhydrate), giving off at the same a large quantity of sulphurous acid. Slight dilution with water destroys the blue colour and precipitates a body having a faint reddish colour, and dissolving in sulphuric acid with the same blue colour. This body gave by analysis numbers agreeing nearly with the formula,  $\text{C}_6\text{H}_6\text{SO}_2$ ; its formation may be represented by the equation—



It is isomeric with phenyl-sulphurous acid, but differs altogether from that acid in its properties.

H. W.

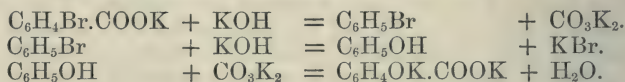
**How is Salicylic Acid formed from the Bromobenzoic Acid melting at 155°?** By H. HUEBNER (*Ann. Chem. Pharm.*, clxii, 71—76).

HUEBNER and Friedburg's experiments (*Zeitschr. f. Chem.* [2], vii, 296) had led them to ascribe the formation of salicylic acid, together with oxybenzoic acid, on fusion of bromobenzoic acid (melting at 155°) with potash—that is to say, of an acid which could not be formed by the direct substitution of the bromine by hydroxyl—to the action of potassium carbonate on phenol, whereas most other chemists regarded the salicylic acid as derived from an isomeric acid present in the bromobenzoic acid. Recently the purity of the bromobenzoic acid employed by Huebner and Friedburg has more especially been called in question by Barth (*Ann. Chem. Pharm.*, clix, 230).

To meet these objections, and obtain further proof of the opinion he had expressed, that no conclusion as to the purity of the bromo-acid employed could be drawn from the formation of several oxy-acids on fusion with potash, the author has once more repeated his experiments, using an acid purified by twelve recrystallisations. Evidence of the great purity of the bromobenzoic acid thus obtained was afforded by the fact that each of the last three crystallisations exhibited the constant melting point of 155°—156°.

It was found, as before, that, in every case, besides oxybenzoic acid, no inconsiderable quantity of salicylic acid was formed,\* and not merely a few milligrams, as stated by Barth.

Other experiments are quoted, showing that when pure phenol is fused with an excess of potash and some sodic carbonate for several hours, salicylic acid is produced. The conclusion therefore seems thoroughly warranted, that salicylic acid is formed from bromobenzoic acid by the following series of reactions:—



H. E. A.

**Amide of Naphthalene-carboxylic Acid.** By P. v. RAKOWSKI (*Deut. Chem. Ges. Ber.*, v, 318).

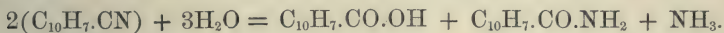
THIS substance is obtained as an intermediate product when naphthalene-carboxylic acid is made by Merz's reaction, viz., action of caustic potash on naphthyl cyanide. Merz observed its production, but considered it to be only naphthalene. It is difficultly soluble in alcohol, is sublimable in yellowish white needles, and becomes red on exposure to air; it melts at 128° as nearly as the small quantity of substance

\* The formation of a small quantity of an acid melting at about 250°—probably *paraoxybenzoic acid*—was also noticed; this acid was not further examined.



obtained permitted the estimation to be made; it is difficultly soluble in boiling dilute sulphuric or hydrochloric acid, and crystallises from these solutions on cooling.

Hofmann obtained an isomeric (?) body, melting at  $244^{\circ}$ , but otherwise agreeing in its properties with this substance, by the action of caustic potash on the nitrile of naphthalene-carboxylic acid (*Deut. Chem. Ges. Ber.*, 1868, 38). The author gives the following equation to represent its production, simultaneously with naphthalene-carboxylic acid :—



C. R. A. W.

**Isocyanuric Acid.** By A. STEINER (*Deut. Chem. Ges. Ber.*, v, 381—384).

WHEN potassium isocyanurate is subjected to electrolysis, it is resolved into  $\text{CO}_2$ ,  $\text{CN}$ ,  $\text{NH}_3$ , and  $\text{KNO}_3$ . Nascent hydrogen acts in a similar way on the acid, and if the action is not allowed to go on too long, there is also oxalic acid formed. By boiling the acid with concentrated hydrochloric acid, it decomposes into carbon dioxide, ammonia, and oxalic acid; the same products are formed by the action of potassium permanganate and lead dioxide; also, but more slowly, by a concentrated potash-solution.

Schischkoff describes an ethyl-ether of this acid; the author, however, was unable to obtain this compound. Liebig also mentions that he did not succeed in obtaining an ether.

The following salts were analysed :— $(\text{C}_3\text{H}_2\text{N}_3\text{O}_3)_2\text{Zn}$  crystallises from a concentrated solution in long needles, soluble in alcohol;  $(\text{C}_3\text{H}_2\text{N}_3\text{O}_3)_2\text{Mg} + 5\text{H}_2\text{O}$  is also soluble in alcohol and crystallises in needles;  $(\text{C}_3\text{H}_2\text{N}_3\text{O}_3)_2\text{Cu} + 4\text{H}_2\text{O}$  crystallises from a concentrated solution in needles, and from a dilute solution in beautiful emerald-green rhombic crystals.

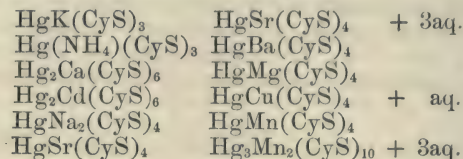
On mixing solutions of isocyanuric acid and mercurous nitrate, a crystalline precipitate is formed which decomposes at a gentle heat, with separation of mercury. Mercuric nitrate gives with the acid a thick gelatinous precipitate, which after some time changes into a crystalline powder having the composition  $(\text{C}_3\text{H}_2\text{N}_3\text{O}_3)_2\text{Hg}$ . A basic salt,  $(\text{C}_3\text{H}_2\text{N}_3\text{O}_3)_2\text{Hg} + \text{HgO}$ , is obtained by dissolving freshly precipitated mercuric oxide in the acid, as a powder resembling lycopodium.  $(\text{C}_3\text{H}_2\text{N}_3\text{O}_3)_2\text{Pb} + 2\text{H}_2\text{O}$  forms long, broad needles, sparingly soluble in cold water and freely in hot water. The manganese salt does not crystallise well, and the ferric salt is obtained as a red-brown powder on adding ether to the alcoholic solution. It dissolves in water to a blood-red liquid, and is left on evaporation as a syrup.

All isocyanurates detonate when heated on platinum-foil.

C. S.

**Double Salts of Mercuric Sulphocyanate.** By TH. NORDSTRÖM  
(*Deut. Chem. Ges. Ber.*, v, 989).

The following were prepared and analysed:—



H. W.

**Optical Properties of Ethylene-diamine Sulphate.** By V. v.  
LANG (*Wien. Anzeiger*, 1872, 28; *Chem. Centr.*, 1872, 178).

THIS compound, though it crystallises in the tetragonal system, exhibits the property of circular polarisation, a peculiarity hitherto observed only in strychnine sulphate. The circular polarisation of the ethylene-diamine salt is about three-fourths that of quartz. The crystals examined were partly dextro- partly lævo-gyrate, but no hemihedral or hemisymmetric forms were observed in them.

H. W.

**Formation of Diphenylamine.** By CH. GIRARD and G. DE LAIRE  
(*Compt. rend.*, lxxiv, 1254).

THE authors are at variance with MM. Dusart and Bardy regarding certain reactions of phenyl-compounds.

Aniline and oxyphenylsulphite of sodium give rise at 300° to diphenylamine, proceeding partly at least, according to Dusart and Bardy, from the phenol of the oxyphenylsulphite. De Laire and Girard attribute it entirely to the aniline.

Dusart and Bardy have announced the formation of benzonitrile from an oxyphenylsulphite and a cyanide, also the production of aniline and diphenylamine from phenyl and ammonium chlorides. The authors could not obtain either of these results.

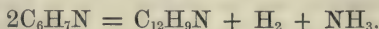
C. G. S.

**Synthesis of Carbazol.** By C. GRAEBE (*Deut. Chem. Ges. Ber.*, v, 976).

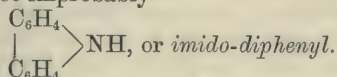
THE author publishes his results, though not complete, on account of the notice recently published by Braun and Greiff on this subject (*Deut. Chem. Ges. Ber.*, v, 276).

Aniline vapour passed through a porcelain tube at a bright red heat forms a small quantity of carbazol, together with hydrogen, ammonia, and ammonium cyanide; the fluid distillate is not wholly soluble in hydrochloric acid; from the residue impure carbazol is readily obtainable by alcohol and sublimation; the picric acid compound was analysed,

and from it pure carbazol obtained by ammonia. Hence the formation of carbazol is expressed by the equation—



and its formula is not improbably—



Hence it might be expected that diphenylamine would yield carbazol even more readily than aniline when subjected to similar treatment, which is found to be the case, sufficient of the picric compound for analysis being obtained when only 10 grams of diphenylamine are employed.

The author proposes to examine the action of acetyl chloride, &c., on carbazol, with the view of obtaining further evidence as to the correctness of the formula ascribed to this body.

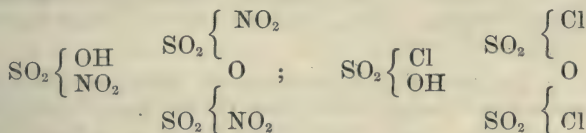
C. R. A. W.

**A Correction.** By C. SCHORLEMMER (Deut. Chem. Ges. Ber., v, 378).

IN the German edition of Roscoe's chemistry, the formula of the lead chamber crystals is given in one place as  $\text{SO}_2 \left\{ \begin{array}{c} \text{NH} \\ \text{NO}_2 \end{array} \right.$ , instead of  $\text{SO}_2 \left\{ \begin{array}{c} \text{OH} \\ \text{NO}_2 \end{array} \right.$ , through a printer's error.

Rammelsberg doubles the empirical formula  $\text{HSNO}_5$ , but the single formula is in harmony with the behaviour of the body to water, which forms sulphuric and nitrous acids.

De la Provostaye's compound is the anhydride of this, just as the chloride of pyrosulphuric (di-sulphuric) acid is the anhydride of chloro-sulphuric acid.



C. R. A. W.

## Physiological Chemistry.

**Physiological and Chemical Action of Phenol (Carbolic Acid) in the Animal Organism.** By E. SALKOWSKI (Pflügers Archiv., 1872, p. 335—358).

PHENOL causes irritation of the part to which it is applied. It increases the reflex excitability of the spinal cord, and produces convulsions similar to those occasioned by strychnine. These are preceded by a transient soporose condition and are accompanied by paralysis in frogs, but this is



not the case in rabbits. The respiratory nervous centre is first stimulated both directly, and through the vagi, and respiration is quickened; but afterwards the centre becomes paralysed, the breathing stops, and death ensues. The beats of the heart are rendered slow in frogs by large doses, but are quickened in man by small doses.

Phenol is absorbed as such and can be detected in the blood. It is partly excreted unchanged in the urine and partly oxidized in the organism, yielding oxalic acid which is found in the blood. The best way of detecting phenol is to add to the liquid containing it  $\frac{1}{4}$  of its volume of ammonia and a few drops of a solution of chloride of lime (1 in 20) and gently warm it, but not to boiling. If much phenol is present, a blue colour at once appears, changing to red when the liquid is acidified. If the phenol is present in small quantity only, the liquid must be allowed to stand for several minutes. Too much heat or too much chloride of lime destroys the reaction. A blue colour is produced by  $\frac{1}{40000}$ th of carbolic acid. The phenol is isolated from the urine, before applying the reaction, by acidifying it strongly with tartaric acid, distilling over half of it with a naked flame, shaking the distillate twice with several volumes of ether, distilling off the ether, dissolving the residue in a few c.c. of water, and filtering if necessary. The reagents are then added.

Phenol seems to be combined with alkali in the urine, as the reaction is not obtained unless the urine is acidified, even although it has an acid reaction. In opposition to Buliginsky, the author finds that phenol acid is prevented by potash from distilling over. The dark colour of the urine, which often occurs after the use of the phenol, is due to some oxidation-product. It occurs more frequently when phenol is used externally than internally, probably from its being oxidized in the former case before absorption. The dark coloration of the urine and the amount of phenol it contains do not correspond at all.

T. L. B.

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**Presence of Phenol in the Animal Body and its Action on Blood and Nerves.** By F. HOPPE SEYLER (*Pflügers Archiv. für Physiologie*, v, 470—480).

THE author confirms the observations of Städeler and Buliginsky, that phenol can be obtained from urine by distilling it with sulphuric acid; also the statement of Lieben, that it can be obtained by simple distillation and rectification. The phenol, however, is not originally contained in the urine, but is formed by the action of the sulphuric acid employed either in the distillation or rectification. The observation of Landolt that bromine-water precipitates directly from urine, tribromophenol, or at any rate a substance which yields phenol when treated with sodium-amalgam (*Journ. of Chem. Soc.*, 1871, p. 1216) is also correct. But bromine-water decomposes paraoxybenzoic acid and yields tribromophenol, and also converts salicylic acid into dibromosalicylic acid, which yields phenol with sodium-amalgam, so that his observation does not prove the pre-existence of phenol in the urine. The substance from which phenol is formed by the action of sulphuric acid is probably indican. Hippuric acid and indican (and the substance which yields phenol, if it be different from indican) are not

found in the blood or organs, but only in the urine, and are therefore formed in the kidneys. The author considers that urea must be formed in the same place as hippuric acid, *i.e.*, in the kidneys, and not, as is supposed by many, in the liver.

Landolt's test for phenol is so good that by distilling with dilute sulphuric acid the blood and tissues of an animal poisoned by phenol, the parts of the body in which it has especially accumulated and proved hurtful, can be easily determined. In one experiment the greatest quantity was found in the kidneys, next came the brain, then the blood, and lastly the liver.

The author relates two cases, in which the external application of phenol for scabies proved fatal to one man, and nearly so to another. The symptoms were tension in the head, giddiness, loss of consciousness, and weak respiration.

The effect of phenol on animals is to cause great dilatation of the blood-vessels, muscular twitches, weak respiration, and lowering of temperature.

These effects can be produced by painting phenol over the skin of the abdomen, and this, together with the demonstration of the presence of phenol in the brain, forms a good lecture experiment for the purpose of showing—(1.) The absorption by the skin of substances which easily permeate it; and (2.) The connection of nervous symptoms with the entrance of the poison into the brain.

T. L. B.

### The Peptones of Fibrin. By J. MOHLENFELD (Pflügers Archiv. für Physiologie, v, 381—401).

WHEN fibrin was digested with artificial gastric juice a slight residue always remained. Its amount was too small to allow of an accurate examination, but it consisted chiefly of saponifiable fats.

The solution was neutralized with baryta and boiled in order to remove the parapeptones and a body observed by Meissner, which is coagulated by heat. The solution was clear, and therefore did not contain Meissner's metapeptone, which would have rendered it turbid. As the fluid was neither rendered turbid by boiling, nor gave a precipitate with potassium ferrocyanide and acetic acid, it did not contain either the *a* or *b* peptone of Meissner.

When it was evaporated and treated with alcohol, leucine and several other substances, whose reactions the author gives, were dissolved out. One of these, though not tyrosine, gives Hoffmann's reaction, and to it the author believes the violet colour produced in solutions of peptones by caustic soda and copper sulphate to be due. After removal of the baryta, silver oxide and alcohol were added to the liquid, when a yellow, cheesy precipitate was produced. This body seems to contain sulphur, but its amount was not determined.

The composition of this substance when combined with and when free from silver corresponds best with the formula,  $\left\{ \begin{array}{l} \text{C}_{41}\text{H}_{81}\text{N}_{14}\text{O}_{20}^{(+8)}\text{Ag}_5 \\ \text{C}_{41}\text{H}_{86}\text{N}_{14}\text{O}_{20}^{(+8)} \end{array} \right.$ .

After removal of the excess of silver from the solution by hydrogen sulphide, succeeded by a stream of H, the liquid was evaporated and

precipitated by the addition of a large quantity of alcohol. The composition of the precipitate corresponds to the formula,  $C_{143}H_{301}N_{40}S_1O_{62}$ . The composition of its barium-compound would indicate that the formula should be doubled, but it is not certain that the amount of barium in the compound is constant. The composition of this body differs much from that of fibrin, but its formation from fibrin could be explained by supposing that 100 equivalents of fibrin took up 16,650 equivalents of water and gave off 15,000 equivalents of  $CO_2$ .

The results of this research show that there is a wide difference in composition between the original albuminous body and the products of its digestion. The second of them, whose formula was reckoned at  $C_{41}H_{86}N_{14}O_{20}^{(+s)}$ , differs much from the albumin in containing a large amount of it, and it is difficult to believe that it is transformed in the blood into an albuminous body. If it were so, the whole process of decomposition in the stomach would be superfluous and the formation of leucine, &c., difficult to explain. It is more likely that this substance, rich in nitrogen, is the first product of the decomposition of fibrin, from which those substances in the organism which contain still more nitrogen, are formed by further decomposition.

T. L. B.

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**Action of Pepsin on the Fibrin of Blood.** By VON WITTICH  
(Pflügers Archiv. für Physiologie, v, 435—469).

A NUMBER of the experiments related in this paper were made by Grünhagen's method (p. 313 of this volume), but as the time when the first drop falls from the filter is influenced by the thickness of the paper employed, &c., the author prefers to take the amount of filtrate in a given time as a measure of the activity of digestion. He determines the total amount of the products of digestion by the lævotation of polarized light in a Soleil-Ventzke's apparatus, and the amount of peptones formed, by neutralising the liquid so as to precipitate para-peptones, and again noting its rotatory power. He assumes that one division of the scale represents 1 per cent. of peptones, or other albuminous substances in solution, with sufficient exactness for comparative experiments. In preparing a glycerin solution of pepsin from the mucous membrane of a stomach, he recommends that the pyloric part should be rejected entirely, as the mucus it contains hinders the filtration of the glycerin extract; and he finds, in accordance with Friedinger and Fick, but in opposition to Haidenhain and Ebstein, that it contains little pepsin. He now finds that pepsin may be extracted from gastric mucous membrane after it has been steeped in alcohol, or from the precipitate which is produced in glycerin extract of fresh mucous membrane by the addition of alcohol. The glycerin must, however, be allowed to remain in contact with the mucous membrane or precipitate for several days, and the negative results which the author formerly obtained were due to his having tested the peptic properties of the glycerin after 24 hours instead of after several days. He is not certain whether pepsin is albuminous or not, for though it does not give the reactions of albumin, this might be due to the excessively small quantity of it present. It differs from albuminous sub-



stances in resisting putrefaction; it agrees with them in being almost entirely indiffusible into distilled water. It diffuses, however, very rapidly into dilute hydrochloric acid of 2 per thousand. He thinks this is due to the formation of a diffusible compound with the acid. Fibrin absorbs pepsin most energetically. When put into water into which pepsin can dialyse, it causes it to pass through the parchment more quickly. An excess of fibrin will absorb from artificial gastric juice all the pepsin which has already digested a part of it, and when the undissolved fibrin is taken out and put into fresh acid, the pepsin it contains is generally sufficient to dissolve both it and additional fibrin added to it, while the liquid from which it has been removed has lost all peptic properties. When, however, fibrin is digested upon a filter, the pepsin runs from the filter together with the products of digestion, so that the amount of pepsin remaining with the fibrin on the filter gradually diminishes, and its digestion consequently becomes slower. This circumstance, as well as the fact that the pepsin becomes diffusible in presence of free acid, causes him to believe that the process of digestion begins by pepsin forming a loose chemical compound with the acid, and that this compound is the active agent in the process. He considers that they combine in definite proportions. Deficiency of acid will stop digestion although pepsin be present.

When fibrin is digested with pepsin, not on a filter but in a glass, so that they remain in contact during the whole time of digestion, the amount of fibrin digested is in proportion to the amount of pepsin added. The rapidity with which digestion begins is dependent in the first place on the amount of pepsin. The rapidity with which digestion is performed increases with the temperature up to about 50° C. It goes on, though very slowly, even at such a low temperature as 3° C., attains its maximum rapidly between 35° and 50°, and above this becomes slower. Schiff's statement that the activity of pepsin is suspended at temperatures under 13° is inaccurate. Exposure to 5° for some hours does not destroy the activity of pepsin. The activity of a dilute solution of pepsin is destroyed by exposure for two minutes to 70°, while that of an undiluted glycerin solution was retained after exposure for the same time to 80°.

When digestion stops before all the fibrin in a digestive solution has been dissolved, the arrest of the process is not due entirely to the accumulation of products of digestion, as the amount of those at the time of arrest is found to vary considerably, but is partly due to the want of free acid. His explanation of this is that a definite amount of pepsin and of acid is requisite for the digestion of a given quantity of fibrin. The fibrin which remains undissolved in an otherwise active digestive fluid, has part of the acid which it has absorbed withdrawn from it during the process of digestion, so that the quantity it retains is too small for its digestion, although it has absorbed all the pepsin which has finished digesting the rest of the fibrin. The presence of water is necessary to digestion, and an insufficient quantity of it retards the action of pepsin.

The proportion of the products of digestion which is necessary to stop digestion in a solution increases with the amount of pepsin present.

The relation between the para-peptones and peptones is not constant, and the former are present only at a preliminary stage in the production of the latter, and are converted into them by an additional amount of pepsin. The amount of peptones formed at the expense of para-peptones increases with the amount of pepsin present.

Digestion is arrested by accumulation of products of digestion, and especially of peptones in the digestive fluid. It is impeded by the presence of 4·3 per cent. of peptones, and probably stopped by 6 or 8·6 per cent.

Dilute acid alone will convert fibrin into peptone, even at ordinary temperatures, but much more slowly than when pepsin is present.

Fibrin soaked in dilute hydrochloric acid till it formed a stiff jelly, and placed in an air-bath at 30°—40° C., became fluid in 24 hours, and contained 1 per cent. of peptone.

T. L. B.

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**Coagulation of Fibrin.** By ALEXANDER SCHMIDT (Pfluger's Archiv., v, 487).

SCHMIDT gives a short abstract of the results of his investigations on this subject.

As soon as blood is removed from the living blood-vessels, a ferment is produced by the action of the corpuscles on the plasma. It is this ferment which causes the coagulation of fibrin. It is absent from the circulating blood. In order to obtain the ferment, the albuminoids of the blood, or blood-serum, are coagulated by the prolonged action (fourteen days at least) of large quantities of strong alcohol, the liquid is filtered, and the residue dried at a low temperature, pulverised, and extracted with water. Glycerin also dissolves the ferment from the moist residue, but in less quantity. The fermentable material consists of fibrinoplastic and fibrinogenic substances. These may be isolated singly, but both must be at the same time subjected to the action of the ferment in order to produce fibrin. The ferment exists largely in blood-serum, and can be precipitated together with the fibrinoplastic substance. The albumin of this precipitate can be entirely removed without affecting the ferment. The slow coagulation of certain kinds of blood depends on the slow development of the ferment. Addition of neutral alkaline salts interrupts the development of the ferment. A low temperature retards the fermentation itself.

The great majority of transudate fluids obtained from the dead body contain both the elements of fibrin, but no ferment, or only traces thereof. There are some transudates, on the other hand, from which fibrinoplastic substance is altogether absent.

The former coagulate on addition of the ferment alone; the latter require also fibrinoplastic substance. The blood-corpuscles contain neither fibrinoplastic substance nor ferment, but they favour the rapidity of fermentation in a remarkable degree, so that they produce in a few minutes the change which, without them, would take hours. This action of the blood-corpuscles is dependent on hæmoglobin. All in themselves indifferent substances, however, which condense oxygen on their surface, and decompose peroxide of hydrogen in a catalytic

manner, have an effect similar to that of hæmoglobin. Thus spongy platinum, charcoal, mercury, even filtering paper, have this influence. Schmidt is continuing his reseaches in reference to rigor mortis, and the effect of injecting the ferment into the circulation of animals.

D. F.

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**The Connective Tissue of Invertebrata.** By A. FRORIEP  
(Pflüger's Archiv., 1872, 320—323).

It is not yet definitely ascertained in how far the connective tissue of the invertebrata corresponds to that of the vertebrata, or in how far it is to be considered as true connective tissue. Microscopical investigation has shown that the embryonal tissue of invertebrata mostly corresponds in appearance to the connective tissue of the vertebrates. Only in some groups is mucous tissue found (Cœlenterata, Vermes, Heteropoda), while the fibrillar tissue is found only in the Cephalopoda, cartilage only in the Cephalopoda, and in the lingual cartilage of the Gasteropoda, while bone does not exist in the invertebrata at all. The question to determine was whether all these tissues really agree with their homologues in the vertebrata in their chemical composition, and whether gelatin might be obtained from them.

A number of vineyard snails were boiled for some time. The decoction did not gelatinise. It was completely precipitated by acetic acid, and hence must be regarded as chondrin, or some similar substance. It could be converted into chondro-glycose by boiling with hydrochloric acid. A similar result was obtained with fresh specimens of Anodonta and Unio.

The Gasteropoda and Lamellibranchiata therefore possess a connective tissue nearly allied to the connective tissue of vertebrates. They differ, however, from the Cephalopoda, for Hoppe-Seyler obtained from these, specimens of pure gelatin free from chondrin.

It was of interest to determine whether the pen of the Sepidæ and Loligidæ contained a substratum of connective tissue.

The salts were dissolved out by hydrochloric acid, and the framework boiled in closed tubes for twenty hours. The decoction did not gelatinise, but became turbid when cold. This substance was insoluble in alcohol, but soluble in acetic acid and sodium acetate. Ferrocyanide of potassium caused no precipitate. The other characters show that the stroma of the sepia-pen is not conchiolin, as might have been supposed from its homology with the shells of molluscs. It would appear that in the cephalopoda the chitin of the Arthropoda and the connective tissue of the vertebrata are combined. No gelatin or similar substance could be obtained from cockchafers, which were under analysis for chitin.

D. F.

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**Physiology of the Bladder and Kidneys.** By DR. TRESKIN  
(Pflüger's Archiv., 1872, 324—335).

TRESKIN seeks to determine what changes, if any, occur in the composition of the urine when it has been allowed to remain some time in



the bladder. Kaupp, who alone seems to have made experiments on the subject, had come to the conclusion that urine which had remained some time in the bladder contained less water and less urea than when secreted, and that the amount of sodium chloride became increased. Treskin thinks that no previous experiments have really shown how much the influence of remaining in the bladder, apart from all other conditions, affects the composition of the urine. The chief point to determine is in what direction diffusion takes place between the blood and the urine, and what constituents are particularly affected. For the purpose of obtaining the urine for the analyses necessary rather serious operations were required. These, which were performed on dogs, consisted in performing lithotomy, and introducing a catheter, by which injections might be made into the bladder, and by which the bladder might be tightly closed or completely emptied when necessary. The urine was obtained direct from the kidneys by tying cannulæ into the ureters. The urine so obtained was analysed before it had reached the bladder, and then again after it had been injected into and remained some time in the bladder.

Tables are given of the analyses in different cases. As the result of the experiments and comparison of the tables, it is concluded—

That the contents of the bladder stand in relations of diffusion with the blood and lymph in its walls, and that, as the result of this, the urine draws to itself water, and gives back urea to the blood. The volume of urine therefore increases, while its specific gravity diminishes to some extent.

As urea, therefore, may pass from the urine to the blood, we must regard it possible that the urea found in the blood may have been primarily formed in the kidneys.

This diffusion also takes place, although the kidneys are secreting a more concentrated urine than that which is contained in the bladder.

Urine which is allowed to stagnate in the bladder, in addition to absorbing water, likewise absorbs chloride of sodium.

From a comparison of the amount of urine and its constituents secreted by the right and left kidneys respectively, Treskin found that, as to quantity of urea, they do not differ appreciably in a given time, although they may differ from each other very considerably as regards the percentage amount.

D. F.

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### Is Sugar a Normal Constituent of the Urine? By I. SEEGEN (Pflüger's Archiv. für Physiologie, 359—374).

SEEGEN has repeated the experiments of Brücke and Bence Jones, the results of which led them to consider sugar as a normal constituent of healthy urine. He discusses the value of the reduction and fermentation tests as evidence of the presence of sugar alone, and believes that neither of these tests for sugar is absolutely indicative of sugar only.

Brücke states that sugar may be obtained from normal urine in the form of sucrate of potash. His method consists in adding alcohol to the urine till the mixture contains four-fifths of absolute alcohol. The precipitate which forms is allowed to sink, and the liquid filtered. To the filtrate an alcoholic solution of potash is added, which after a

time causes a crystalline deposit on the sides and bottom of the vessel. This deposit is regarded by Brücke as chiefly composed of sucrate of potash. Seegen has obtained the same deposit, but never could get any true reduction of copper sulphate by this substance. He shows by experiments on sugar solutions of known strength, that it is quite impossible to obtain sucrate of potash by Brücke's method, owing to the alcohol being in too small amount. He shows that even if it is present it is not precipitated, unless there is 90 per cent. of alcohol in the solution. In such case it is precipitated at once as a yellow varnish-like mass, which turns brown on exposure to the air. It has no crystalline characters.

Brücke's sucrate of potash is therefore only a compound of potash and some of the urinary constituents.

The other method by which Brücke sought to demonstrate the presence of sugar was to precipitate urine first with lead acetate and then with lead subacetate and ammonia. The precipitates by the last two reagents contained the sugar, which was set free, and subjected to the fermentation test. In this way he succeeded in getting an evolution of carbonic acid, which was considered as due to the fermentation of sugar. Seegen shows that none of these precipitates gives the reduction of copper in a manner characteristic of sugar. He attributes the indistinct reduction which occurs to the uric acid, which is carried down principally with the subacetate, and in smaller amount by the ammonia.

He failed to obtain fermentation from any of these precipitates. He criticises the results obtained by the fermentation test; and by a comparison of the methods of carrying out the fermentation test, by experiments as to what is the smallest amount of sugar that will give a satisfactory result, by testing the results obtained by a simple mixture of yeast and water, and by simply leaving urine without any addition of yeast, he arrives at the conclusion that the minute amount of carbonic acid which has been looked upon as the result of the fermentation of sugar, is due to the decomposition of some of the urinary constituents, or of the yeast itself.

He thinks that the presence of alcohol as one of the products of fermentation is not necessarily a proof of sugar, and considers that the method of Bence Jones is not delicate enough to distinguish between the amount of alcohol obtained from a mixture of yeast and water only, and that from a liquid containing only the minute quantity of sugar indicated by the test (0.0002 per. cent.). Huizinga's reaction with iodoform is liable to the same objection.

Kühne gives the normal amount of sugar in the urine as 0.1 per cent. This seems to Seegen a most unaccountable statement, inasmuch as urine containing only 0.05 — 0.03 per cent. of sugar will give all the sugar reactions quite plainly by the lead precipitates.

Seegen considers it proved, therefore, that sugar is not a normal constituent of the urine.

D. F.

**A Method of determining a Minimum Amount of Sugar in the Urine.** By I. SEEGEN (*Pflüger's Archiv.*, v, 375—380).

TROMMER'S test, the most delicate test for sugar, is liable to two objections in testing for sugar in the urine:—

(1.) The urinary constituents obscure the reaction; the precipitation of the cuprous oxide is hindered or rendered incomplete; and instead of the characteristic reduction in minimum watery solutions of sugar, only a yellow coloration or a dichroic turbidity is obtained in urine containing a similar amount.

(2.) Some urinary constituents, and especially uric acid, likewise reduce copper; and in urine rich in uric acid it is doubtful whether the reduction is due to the presence of sugar or to a large amount of uric acid.

Seegen finds that one of these objections is removed by filtering the urine several times through animal charcoal. Urine after two or three filtrations becomes clear like water. The sugar-containing filtrate gives a better reaction than the original urine, but it is not yet quite freed from substances which hinder the reduction. The reduction is, however, very characteristic, when after complete filtration the charcoal on the filter is washed with a little distilled water and the wash-water employed for the reaction. This gives the reaction better than the filtrate. The reaction is not equally sensitive for all kinds of urine.

Urine of a pale colour and comparatively low specific gravity (1.018) gives the reaction better than more highly coloured urine richer in uric acid, if the sugar is in minimum amount. If it is in larger quantity, the wash-water is very sensitive to the reaction. In these cases the water of the second or third washing gives the characteristic reactions better than the first. The reason for this is that the substances which hinder the reduction of the copper either pass into the filtrate or are held back by the charcoal and not washed out of it with the sugar.

The second point was to determine whether the better reaction of the charcoal washings was due to a larger amount of uric acid. A watery solution of uric acid corresponding to the amount contained in the urine when filtered through charcoal produced no change in the copper solution, nor had the washings any effect. The sensitiveness of Trommer's test for uric acid is not so great as for sugar. With this test 0.3 milligrams of sugar may be detected after 10,000 times dilution, while with 5 c.c. of a like strength, 0.01 per cent. solution of uric acid, have only a very faint action on copper. The reduction of copper by the filtrate or washings is not due to uric acid.

Most kinds of urine render Fehling's solution yellow when boiled with it without causing a precipitate. This is not always due to uric acid. The nature of the substance which causes this result is, however, not known.

The method of filtration through animal charcoal must not be employed if the quantity of sugar is to be estimated, as the charcoal retains a part of the sugar which cannot be removed by washing either with hot or with cold water.

D. F.



**Is the Absolute Amount of Acid in the Urine greater on a day of Exertion than on a day of Rest?** By A. SAWICKI (Pflüger's Archiv., 1872, 285—290).

KLÜPFEL states that the amount of acid in the urine on a day of exertion is on an average 44·8 per cent. greater than on a day of rest. The results arrived at by Sawicki do not agree with these statements. The exertion consisted in long walks and the use of dumb-bells. The quantity of acid was determined by neutralisation with semi-normal solution of caustic soda. Several individuals were the subject of experiment, and the results are stated in a tabular form. For particulars reference must be had to the original. The tables, however, show no correspondence between the amount of exertion and the amount of acid in the urine. The same is true of the amount of phosphoric acid. The author does not consider that the question of the acidity of the urine during work and rest has been definitely settled by his experiments, but thinks his results undoubtedly prove that the amount of acid is more dependent on the quantity and quality of the food than on the state of the body as to work or rest.

D. F.

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**Respiration of Fishes.** By N. GRÉHANT (Compt. rend., lxxiv, 621—624).

THE author has made experiments similar to those of Humboldt and Provençal on the respiration of fishes, but he makes use of the mercury-pump to extract the gases from the water, and has obtained results partly at variance with theirs. He has found, firstly, that fishes (tench) evolve a volume of carbonic anhydride equal to that of the oxygen they absorb. Humboldt and Provençal found it to be only four-fifths of this. Secondly, that they exhale nitrogen (according to Humboldt and Provençal they absorb it); thirdly, that when deprived of their swimming bladder they exhale a volume of carbonic anhydride greater than that of the oxygen they absorb, and that they absorb no nitrogen. Humboldt and Provençal found that under this condition much nitrogen was absorbed and no carbonic anhydride exhaled.

He has also found that fishes can remove the whole of the oxygen dissolved in water, and that they can deprive oxidised hæmoglobin of its combined oxygen. Thus he has observed that fishes live longer in the same kind and quantity of water when it is mixed with some defibrinated oxygenated blood than when it is not, and that they reduce the oxidised hæmoglobin. The author regards this observation as of importance in general physiology, inasmuch as it illustrates the mode in which the respiration of the mammalian foetus is effected in the maternal placenta.

E. D.

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**On the Changes which Oxybenzoic and Paroxybenzoic Acids undergo in the Blood.** By R. MALY (Chem. Centr., 1872, 181).

OXYBENZOIC acid and paroxybenzoic acid were found, after administration, in the urine along with a glycocine group, but the substances met

with were not identical with those found after administration of the isomeric body, salicylic acid.

T. S.

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**The Bile Pigments.** By R. MALY (Chem. Centr., 1872, 180).

A CONTINUATION of two previous communications to the Vienna Academy. The preceding papers related to the oxidation-products of the bile-pigments, this to the action of reducing agents on bilirubin. Nascent hydrogen from sodium amalgam converts bilirubin into *hydrobilirubin* ( $2\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_3 + \text{H}_2 + \text{H}_2\text{O} = \text{C}_{32}\text{H}_{40}\text{N}_4\text{O}_7$ ), identical with Jaffé's urobilin obtained from urine, so that the transition of bile-pigment into urine-pigment is established experimentally. In the intestine bilirubin is under the influence of reducing agents, notably of hydrogen.

In its fluorescence, the colour of its acid and alkaline solutions, its diffusibility, the peculiarities of its combinations with metals, and in the characteristics of its absorption spectra, hydrobilirubin agrees exactly with urobilin. By its spectrum it may be recognised in the blood.

T. S.

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**Physiological Action of Formic Ether.** By H. BYASSON (Compt. rend., lxxiv, 1202).

FORMIC ether inhaled by rats, guinea-pigs, or dogs causes asphyxia, accompanied by a considerable diminution of temperature. As an anæsthetic it cannot be compared to chloroform; its action is less rapid; it produces less insensibility, and the animals do not return to their normal state for several hours. A sub-cutaneous injection of 1 to 2 c.c. for rats and guinea-pigs, and 4 to 6 c.c. for dogs produces somewhat similar results. A dose of 6 to 8 grams causes in men a marked tendency to sleep, and formic acid is found in the urine; other phenomena have not been ascertained.

Under the same conditions acetic ether produces no marked results.

The special physiological action of hydrate of chloral is considered by the author to be due to the combined action of chloroform and formic acid, which products are formed in the body under the influence of the alkaline carbonates of the blood.

J. B.

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**Antidotes to Poisoning by Phenol.** By TH. HUSEMANN (Chem. Centr., 1872, 36).

THE author finds that the best antidote to phenol is sugar-lime (prepared by dissolving 16 parts of loaf-sugar in 40 parts of water, adding 5 parts of slaked lime, filtering after frequent agitation and evaporating at 100°. Calcium carbonate is less efficacious. Fixed oils, as olive-oil or almond-oil, recommended by Calvert, were not found by the author to produce any good effect.

H. W.

## Chemistry of Vegetable Physiology and Agriculture.

**On Pollen and the Formation of Wax.** By W. VON SCHNEIDER  
(Ann. Chem. Pharm., cxii, 235—258).

BEES collect from flowers two substances, nectar and pollen. With regard to the former, the author considers the question whether the sugar it contains undergoes chemical change during the preparation of honey, as still unsettled. Books generally indicate among the constituents of honey a nitrogenous substance. Blume found nitrogen in honey and thinks this the reason that bees may live for some time upon honey alone. In one specimen of honey extracted, direct from the comb and examined by the author, no nitrogen could be detected, but on the other hand he found, in impure purchased samples, variable quantities of nitrogen. This, however, undoubtedly proceeded from impurities.

After quoting at length older analyses of the pollen collected by bees, and known as "bee-bread," the author describes in detail his own examination of this substance. His experiments were conducted upon two kinds obtained from two different districts. A qualitative examination led to the conclusion that the nitrogen was partly in the form of albumin and partly in the form of peptones.

The results of the quantitative analysis are as follows:—

Water.....	29.89	p. c.
Ash (chiefly alkaline phosphate) .....	3.08	"
Albumin and peptones.....	17.81	"
Sugar.....	25.12	"
Fat, fat acids, cerotic acid, myricin, oleic acid, } colouring matter .....	8.98	"
Cell-membrane.....	7.56	"
Pectin .....	7.42	"
	99.86	"

The author concludes, from the results of this analysis which represents the proportion of waxy matters in pollen as very small, and from experiments upon the consumption of food by bees in comparison with the wax produced, that bees do secrete wax, and that it is not brought into the hive with the pollen which they collect.

This conclusion is in accordance with the statements of naturalists, that bees supplied with honey free from wax produce wax in a short time, and that by addition of pollen to wax-free honey the production of wax continues permanently.

W. A. T.

**Physiological Chemistry of Lichens.** By W. KNOP (Chem. Centr., 1872, 172—176).

BESIDES offering explanations of some points in the chemistry of lichens, the author describes a new resinoid acid obtained from *Parmelia saxatilis* (Wallroth), *Lobaria adusta* (Hoffmann).



This acid, which he names *lobaric acid*, crystallises in warty masses of thin plates. It is colourless, and in its degree of solubility in different menstrua and in other of its properties it is like a crystalline resin. It is not affected by prolonged exposure to ammonia gas, but dissolves in either aqueous or alcoholic ammonia, forming a colourless solution, which turns rose-red on exposure to the air, and dries up to an amorphous violet-brown mass, resembling in tint the thallus of the lichen which yields it. It dissolves in caustic potash with a pure yellow colour, which on exposure and evaporation changes like the ammonia solution to rose-red and brown-violet. When heated it fuses, evolves dense inflammable vapours, and chars. It has the composition expressed by the formula  $C_{17}H_{16}O_5$ , that of evernic acid being  $C_{17}H_{16}O_7$ .

The author attributes the colour of the brown variety of *Parmelia saxatilis* to the presence of oxidation-products of the potassium salt of lobaric acid. The colour is only superficial, and is produced by the action of the potash derived from the weathering of the granite upon which the lichen grows.

According to the author the ashes of lichens contain alumina. He considers this to be dissolved out of the dust which settles on the lichen and firmly adheres to its surface after wet weather, by the oxalic acid which is known to be a frequent constituent of lichens, this acid being one of the best solvents of alumina. He also thinks it probable that the oxalic acid in lichens is produced during the growth of the plant from what he names the "lichen acids;" for treatment of these acids with caustic alkalis produces a carbonate or an oxalate.

Referring to the researches of Schwendener, from which lichens appear to be not distinct plants but combinations of fungi with algæ, the gonidia of the lichen consisting of algæ that have become enclosed in the hypha (mycelium) of a fungus which then grows into the thallus of the lichen, he points out that the lichen acids are found exclusively in the cortical layers of the lichen, that is, in the fungus, and not in the alga (gonidium).

Respecting the nutrition of the two elements of a lichen, he considers that on the one hand the alga (gonidium) which in many lichens is completely enclosed within the fungus, obtains its nutrient matters through the fungus, by which they are absorbed in damp weather from the barks of trees or the stones on which the lichen grows, and on the other, that the fungus, which cannot be converted into a lichen without the presence of an alga, and cannot of itself fix carbonic anhydride, has its food elaborated for it by the alga.

Lastly, he suggests that the detection of a particular lichen acid in the soridia of lichens may aid in determining the lichen to which they belong.

E. D.

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#### Action of Oxygen on Vegetable Infusions. By the Abbé LABORDE (Compt. rend., lxxiv, 1201).

VEGETABLE infusions kept for a month in a closed vessel in presence of oxygen undergo no change, even although the oxygen may be in the

nascent state. Similar infusions exposed to the air become mouldy in five or six days. This confirms Pasteur's germ theory.

J. B.

**Assimilation of Ammonia by Yeast.** By M. GRIESSMAYER  
(Compt. rend., lxxiv, 1202).

THIS is a short argument in support of Pasteur, and in opposition to Liebig, the former of whom asserts that yeast during fermentation can derive from ammoniacal salts the nitrogen necessary to its life.

J. B.

**On Bacteria.** By FERD. COHN (Chem. Centr., 1872, 186—188).

THIS paper contains an excellent summary of the author's in great part well-known views relative to bacteria. Cohn also states that he finds, in opposition to the statements of Wyman and Crace Calvert, that the development of bacteria in prepared solutions is entirely prevented by exposing these to a temperature of 75°—80°, whilst a temperature of 70° is insufficient. *Penicillium* spores are not destroyed at the above temperatures.

T. S.

**Statics of Industrial Culture.** By M. A. MUNTZ (Compt. rend., lxxiv, 1044—1045).

THE author has instituted a series of experiments with the object of ascertaining, 1stly, the nature and quantity of the elements which are removed from the soil by a crop of hops; 2ndly, the proportion in which the various elements are assimilated by the hop plant during the different phases of its growth.

The following analyses, in which special attention has been bestowed upon the separation of the alkalis, were made of hop plants gathered on the 17th of September from a hop garden at Woerth, at the base of the Liebfrauenberg (Bas Rhin):—

	2,400 plants grown on 38 acres contain	6,316 plants grown on 1 hectare contain
	kilograms.	kilograms.
Water .....	4282·560	11270·270
Carbon .....	997·224	2624·361
Hydrogen .....	119·904	315·547
Oxygen .....	764·304	2011·393
Nitrogen .....	34·633	91·141
Phosphoric acid .....	8·625	22·699
Magnesia .....	9·254	24·352
Potash .....	15·888	41·812
Soda .....	0·173	0·455
Mineral matter not determined....	50·635	133·278
	6283·200	16535·308

R. S.

**On the Mineral Matter of Plants.** By A. BAUDRIMONT (Compt. rend., lxxiv, 877—879).

A LARGE class of plants appear to grow vigorously upon bare rock. The author obtained a number of such plants in a fresh state, and determined the amount of water and mineral matter which they contained. The ash bore in all cases a considerable proportion to the organic matter, though often forming but a small fraction of the entire plant. A selection of the results is given below:—

Name of Plant.	Water.	Organic matter.	Ash.
Cactus peruvianus .....	94·83	4·62	·55
Cactus quinquangularis .....	88·46	9·28	2·26
Agave gigantesque .....	88·38	10·85	·77
Crassula lactea.....	90·92	7·80	1·28
Sedum calcareum .....	87·81	9·19	3·00
Portulacca oleracea.....	90·96	7·00	2·04
Semper-vivum arboreum.....	89·12	8·63	2·25
Aloes.....	79·63	17·68	2·69
Opuntia volutina .....	92·19	4·85	2·96

R. W.

**Feeding Value of Serradella Seed.** By HELLRIEGEL (Annalen der Landwirthschaft, Wochen-Blatt, March 24, 1871).

THE mean analysis of seed from three harvests was as follows:—

Water .....	10·0
Albuminoids.....	22·3
Non-nitrogenous extractive matter ....	37·2
Fat.....	6·0
Crude fibre .....	21·0
Ash .....	3·5
	100·0

The composition resembles that of other leguminous seeds.

R. W.

**Use of Lupine Seed as Fodder.** By H. SETTEGAST (Annalen der Landwirthschaft, Wochen-Blatt, June 7, 1871).

THE general composition of yellow and blue lupine seed is as under:—

	Yellow lupine.	Blue lupine.
Water.....	10·4	13·2
Albuminoids .....	37·5	22·0
Non-nitrogenous extractive matter....	27·3	43·8
Fat .....	4·4	5·6
Crude fibre.....	16·4	12·2
Ash.....	4·0	3·2
	100·0	100·0

As lupine seed is rich in nutritive matter, and can, moreover, be grown on a poor soil, it would be of great value as a feeding material but for the bitter principle (the volatile alkaloid) which it contains.



The presence of this substance renders lupine seed distasteful and injurious to animals, especially to pigs; sheep are but little affected by it. The blue lupine seed is more objectionable than the yellow. The amount of alkaloid present varies a good deal. The alkaloid may be more or less removed by baking the seed in an oven or kiln; or by steeping in water and washing; or by treatment with dilute hydrochloric acid, washing, and then boiling with a little sodium carbonate.

R. W.

### **Examination of Fresh and Commercial Poultry Dung.** By FAUSTO SESTINI (Versuchs-Stationen Organ., xv, 2—9).

FRESH poultry dung contains 64.19 per cent.  $\text{H}_2\text{O}$ , 1.32  $\text{NH}_3$ , .2 N in organic combination, 1.22  $\text{P}_2\text{O}_5$ , .89  $\text{K}_2\text{O}$ . The commercial substance contained as an average 21 per cent.  $\text{H}_2\text{O}$ , .22  $\text{NH}_3$ , and 2.5 N in organic combination; the latter high percentage was due to admixture of feathers.

It was found that poultry dung, allowed to dry slowly in the air, lost during a month  $\frac{5}{6}$ ths of its ammonia. From experiments made with green vitriol, gypsum, and brick-clay, it was found that the former is most effective in preventing the loss of ammonia, and at the same time preserves the dung from becoming mouldy.

E. K.

### **Relation between Absorption, Weathering, and Fertility of Soils.** By R. BIEDERMAN (Versuchs-Stationen Organ., xv, 21—50).

THE author compares the analysis of twenty-three soils by Knop and himself, more especially in relation to their absorptive power for ammonia, and the quantity of the bases of the decomposable silicates. These last, which are taken as a measure of the degree of weathering of a soil, are obtained by digesting 2 grams of the soil with 50 c.c. of 5 per cent. hydrochloric acid, 50 c.c. of water, and 1—2 grams of chromic acid, until the humus is oxidised. The residue from this treatment, together with the carbonates and sulphates, subtracted from 100, gives the bases of the decomposable silicates: they ranged in these soils from 1.8 to 13.42 per cent., and the absorption-number from 8 to 135. In sixteen of the soils, the absorption increased in the same order as the decomposable silicates, the ratio between the absorption number and the latter being as 1: .1— .15. In a few cases the relation between the absorption and the total matters soluble in dilute hydrochloric acid is nearer than between the absorption and decomposable silicates; in these the quantity of calcium carbonate was small, and probably did not originally exist in the soil, but was produced during the weathering process. The portion of the soil soluble in dilute hydrochloric acid, and the loss on ignition, increase in a marked relation to each other; a circumstance which is not surprising, as by weathering the quantity of hydrated silicates is augmented; moreover the greater capacity of bearing crops which the weathered material possesses, tends to add to the humus and hygroscopic water.

When the practical value of the soils was known, it was generally found to increase in the same order as the absorptive power.

Attention should be given, in the examination and analysis of a soil, to those qualities which have a *permanent* value, rather than to the quantities of the separate constituents which can be supplied by manuring, and are altered in quantity and relation to each other by the crops. Among the physical properties which should be studied, are the degree of weathering of the fine earth, the hygroscopic power, the relation to heat, the capacity of retaining water, the ratio of the fine earth to the coarse portion, and the nature of the matrix of the soil. If a coefficient of value could be given to each of the factors of fertility in a similar manner as is now done for absorption, it might become possible, by addition of the numbers, to place soils in well characterised classes, according to their values.

E. K.

**Analysis of Nile Mud.** By W. KNOP (Versuchs-Stationen Organ., xv, 13—21.)

THE air-dried deposit of the Nile contains—

Hygroscopic water.....	5.70
Chemically combined water..	7.63
Humus .....	1.17
Mineral matter .....	85.50

---

100.00

The ash contains:—

CaSO <sub>4</sub> .	CaCO <sub>3</sub> .	MgCO <sub>3</sub> .	SiO <sub>2</sub> .	Sesquioxides.	Monoxides.	
1.30	4.00	0.28	57.00	35.20	2.22	= 100
<hr/>						
94.42						

Silicates insoluble in dilute hydrochloric acid, 81.00.

Bases of the decomposable silicates, 94.42 — 81 = 13.42.

Absorption, 135. The processes of analysis employed are those given in the author's *Bonitirung der Ackererde*. Humus is determined by calculation from the amount of carbonic acid given off on oxidation of the organic matter with chromic acid. In this operation, cork and caoutchouc stoppers are liable to become oxidised, owing to the evolution of ozone. The absorption is determined with a solution of ammonium chloride so titrated that 1 c.c. is equivalent to 1 c.c. nitrogen at 0° C., and 760 mm. 100 grams of the soil are shaken with 200 c.c. of this solution and 5 grams of powdered chalk during forty-eight hours; the ammonia is estimated in 20 c.c. of the filtrate, and calculated for the 200 c.c. The absorption-number, therefore, gives the number of c.c. of nitrogen absorbed in the form of ammonia by 100 grams of the soil.

The small quantity of humus contained in Nile mud, together with its very high absorptive power, and contents in decomposable silicates, give another proof that fertility is due to the mineral constituents of soils, and increases with the absorptive power, which latter, in its turn, augments with the quantity of the bases of the decomposable silicates.

A high percentage of humus shows rather that the soil previously possessed the qualities necessary to fertility.

E. K.

## PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XXII.—*New Tests for some Organic Fluids.*

By J. ALFRED WANKLYN, Corresponding Member of the Royal Bavarian Academy of Sciences.

IN the course of the investigations connected with the establishment of the ammonia process of water-analysis, it soon became apparent that Chapman, Smith, and myself had in our possession a new instrument of chemical research, and in using this instrument I have, I believe, come across some very characteristic properties of the commoner animal fluids. When an animal fluid is mixed with excess of potash, evaporated down in contact with the alkali, and then maintained at a temperature of about  $150^{\circ}\text{C}$ . for some time, it evolves a certain fixed proportion of ammonia. This having been accomplished, a further quantity of ammonia may be got by boiling the residue with alkaline solution of permanganate of potash. Now, for certain animal fluids, the quantity of ammonia yielded by a given weight or volume of the animal fluid is characteristic; and the relative quantities of ammonia obtained by potash and by permanganate of potash are likewise characteristic. Thus are provided two new criteria of these animal fluids, which may become of some importance in practical biology, and especially in some of those enquiries which the medical jurist is called upon to conduct.

My investigations on this subject are far from complete, but still they are sufficiently advanced to enable some idea to be formed of the scope and possibilities of such work.

Of all the animal fluids, I know of only one which yields a large proportion of ammonia to caustic potash, and that fluid is urine. On the other hand, urine is distinguished by the smallness of the yield of ammonia to permanganate of potash.

Milk yields about half as much ammonia to potash as to permanganate of potash.

Blood yields about one-fifth as much ammonia to potash as to permanganate of potash.

White of egg, moist, just as it occurs naturally, gives about one-fourth as much ammonia to potash as to the permanganate.

Gelatin, strange to say, gives no ammonia (or only the least trace) to potash, and a good quantity to permanganate.

It is, moreover, a fact, pregnant with interest, that if the preliminary heating to  $150^{\circ}\text{C}$ ., with caustic potash be omitted, and if the boiling



with permanganate be at once proceeded with, only that quantity of ammonia is obtained which would have been yielded to permanganate of potash if the entire process had been gone through. I have, in another place, insisted upon this being interpreted to mean that casein and albumin are chemical compounds into which urea enters as a constituent part, and that gelatin contains no urea.

I will next give the experimental numbers.

100 cubic centimeters give—

Name of fluid.	Ammonia by potash at 150° C.	Ammonia by perman- ganate of potash.
Urine (human) .....	0·90 gram.	0·05 gram.
Milk of cow .....	0·13 „	0·28 „
Blood of sheep .....	0·46 „	2·20 „
Liquid white of egg (hen) .....	0·32 „	1·30 „
Dry solid gelatin (100 grams) .....	0 „	10 „

These numbers must be looked upon as fair approximations, and may require a little rectification in the progress of the enquiry.

With regard to the possible applications of this work to the elucidation of questions before the medical jurist, I would suggest, just as an instance, the possibility of distinguishing between a spot of milk and a spot of white of egg on a cambric handkerchief, for these investigations are appropriately carried out on minute quantities.

In conclusion, it may, perhaps, be useful to state, that in the above experiments, 5 c.c. of the animal fluid were mixed with water in a 500 c.c. flask, and diluted up to the 500 c.c. mark, thereby forming a dilute solution, whereof 1 c.c. contained  $\frac{1}{100}$  c.c. of the animal fluid; that 5 or 10 c.c. of this dilute liquid were usually taken for one experiment, and that a delicate little retort fitted to a delicate little Liebig's condenser was employed. The retort was heated in an oil-bath. The ammonia was measured by the Nesler test. Further details of this kind of work may be found in the little book on Water-Analysis, by Chapman and myself.

### XXIII.—*Dendritic Spots on Paper.*

By ARCH. LIVERSIDGE, Assoc. R. S. Mines; Scholar of Christ's College, Cambridge.

MINUTE markings of a more or less dendritic or plumose character have long been noticed upon certain specimens of paper, but until the present

they seem to have been examined only by a few botanists and microscopical observers, and they, apparently, have not arrived at any very definite or satisfactory conclusion as to the nature of such dendritic markings.

Agardh and Lyngbye named the spots "*Conferva dendritica*," and Schumacher placed them amongst the fungi under the name of "*Dematium olivaceum*."

From their resemblance, when viewed under the microscope, to the well known dendritic markings found on many rocks and fossils, I was induced to make a chemical examination of them, but was much hindered in my endeavours to do so by the great difficulty experienced in finding sufficient material to work upon with any satisfaction; and the small quantity eventually obtained was by no means in a convenient form, since the dendrites are so thoroughly incorporated with the structure of the paper in which they are found.

Since I found it impossible to procure the dendritic markings in sufficient quantity to enable me to make a thorough chemical analysis by the wet way, I had to content myself with a careful blowpipe examination, supplemented by such special tests as could be applied.

The ash yielded by the spots tinges the outer blowpipe flame with the well-known green imparted to it by copper compounds, and on moistening with hydrochloric acid, the peculiar and unmistakable vivid blue colour due to cupric chloride is at once obtained.

In the borax-bead the reactions are also those of copper, viz., a green bead when hot, changing to blue on cooling.

When several spots are treated in a small test-tube with a little strong ammonia-solution the liquid becomes of a blue colour.

The copper is evidently in combination with sulphur, for on placing a spot on a bright surface of silver, and moistening with hydrochloric acid, a dark stain is produced; this is also the case when several are fused with sodic carbonate, and the resulting bead is placed on such silver surface; sodic sulphide is formed, and this reacts with the silver to form a black stain of argentic sulphide. And, in addition, when they are treated with hydrochloric acid and pure zinc free from sulphur, sulphuretted hydrogen is evolved, which blackens paper moistened with solution of plumbic acetate.

The generation of sulphuretted hydrogen is, of course, favoured by the presence of the nascent hydrogen; this influence of nascent hydrogen is well shown when copper pyrites is treated with hydrochloric acid and zinc, when the pyrites dissolves rapidly, with copious evolution of sulphuretted hydrogen; before the zinc is added, the pyrites dissolves but slowly, even with concentrated acid.

The spots are soluble in solution of ammonia, the liquid acquiring a blue tinge.

Since it was found impossible to separate the material of the spots entirely from that of the paper, but only partially, comparatively large portions of the same paper were submitted to the like treatment, but neither copper nor sulphur was found. Most papers, however, contain sulphuric acid in combination: hence the presence of sulphur in the spots cannot be made out by dissolving them in nitric acid, and then testing for sulphuric acid.

These dendritic markings usually appear to pass through the substance of the paper, and are then found developed on both sides of it; when this is the case, both sides are seldom equally well developed.

In the centre, from which the dendritic branchings radiate, there is commonly a dense nucleus of a much darker colour, which, when rubbed with a hard and smooth body, becomes more or less burnished, and in a few cases after burnishing, the nucleus has presented a bright metallic surface as of copper or brass.

From the foregoing I trust that I have made it quite clear that in chemical composition these dendritic growths do not bear any resemblance to anything of a vegetable nature, and their origin is, I think, made quite plain by the specimen which accompanies this paper; in the centre is observed a minute particle of a yellow metal, from which incipient dendritic ramifications are seen to proceed; such particles appear to have been detached from the paper-making or finishing machinery, and have combined with sulphur, and perhaps with oxygen also, and crystallised out, that is if they be regarded as true crystallisations.

Other markings, known as iron-mould, also having a more or less arborescent outline, are found in paper, especially in old books; these have had their origin in small particles of iron which have become oxidised. This form is not so common now, owing to the improvement made in paper manufacture, such particles being now removed from the pulp by means of magnets; still they are occasionally found, and if the oxidation has not proceeded too far, a microscopic fragment of iron may be found acting as nucleus; this can be detached by means of a needle, or other sharp-pointed instrument, and picked up by a magnet, to which it at once flies. Such a particle answers to all iron tests.

The formation of both kinds of dendrites is greatly favoured by the presence of moisture.

In addition to these two dendritic growths, of undoubted inorganic origin, there are others found upon paper which are of a truly vegetable nature, but they cannot well be mistaken one for the other.

I much regret that it was impossible to make a quantitative determination of their composition.

It should be mentioned that I published a preliminary note upon this subject in "Science Gossip" for April, 1869, but since that time I have had further opportunities of finishing this little investigation.

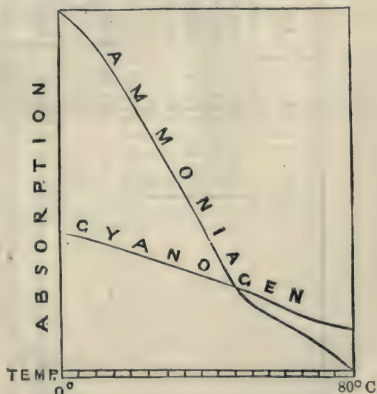


XXIV.—On the Effects of Temperature on the Absorption of Gases by Charcoal.

By JOHN HUNTER, M.A., F.C.S., F.R.S.E.

THE following paper refers to some experiments instituted for the purpose of determining the effects of variation in temperature on the amount of ammonia and cyanogen absorbed by one volume of cocoa-nut charcoal. The results contained in a former communication (*Chem. Soc. Jour.*, March, 1870) indicate that when a gas is capable of being largely absorbed by charcoal, it exists in a partially liquid state within the pores. The question then arises : does the absorption diminish regularly as the temperature increases, or does it change abruptly at a definite point ?

In conducting these experiments, the tube containing the gas and charcoal was surrounded by an external glass vessel, and after the absorption had been determined in the usual way, this was filled with water maintained at a constant temperature, usually commencing at about  $75^{\circ}$  or  $80^{\circ}$  C., until the volume of the residual gas remained constant ; and by making similar observations at intervals of  $5^{\circ}$  C., until the temperature was reduced to zero, a series of corresponding absorptions was obtained. It was found that the volume of ammonia absorbed gradually and continuously decreased as the temperature increased from  $0^{\circ}$  to  $55^{\circ}$  C., but above that point a sudden change occurred, and the successive quantities of the gas given off were considerably less in proportion. In the case of cyanogen, the absorption is continuous between  $0^{\circ}$  and  $80^{\circ}$  C., diminishing as the temperature rises. These results prove that when an easily condensed gas is driven from the pores of the charcoal by the action of heat, it does not escape in a regular curve, but exhibits a rapid change at a certain temperature, and there is no reason to doubt that any largely absorbed gas or vapour will present similar phenomena. Cyanogen probably varies from the regularity of the curve, at a temperature higher than that to which it was exposed in these experiments. By measuring the temperatures on the horizontal, and the volumes on the vertical scale, we obtain a line or curve representing the gradual change in



## AMMONIA (V).

*Temperature per cent.*

	0°.	5°.	10°.	15°.	20°.	25°.	30°.	35°.	40°.	45°.	50°.	55°.	60°.	65°.	70°.
	178.7	167.7	159.7	159.4	147.5	143.5	135.9	127.0	115.3	106.9	95.9	90.8	89.0	88.4	82.6
	172.9	167.0	166.8	155.7	146.9	139.1	130.0	118.9	114.4	101.1	91.9	89.6	87.3	84.3	—
	178.1	171.1	159.6	157.9	148.6	138.0	127.0	121.9	110.3	104.8	100.2	—	90.3	86.6	—
	176.3	173.2	162.9	158.7	148.7	140.6	137.1	121.9	110.5	—	—	—	—	—	—
	178.4	169.3	164.1	157.3	147.9	143.8	131.0	118.0	120.0	—	—	—	—	—	—
	170.3	171.6	165.5	—	148.8	139.4	132.8	119.6	—	—	—	—	—	—	—
	—	170.2	166.1	—	148.7	137.0	129.6	—	—	—	—	—	—	—	—
	—	—	—	—	—	139.5	—	—	—	—	—	—	—	—	—
Average .....	175.7	169.6	163.8	157.6	148.6	140.1	131.9	123.0	114.1	104.2	96.0	90.2	88.1	86.4	82.6

## CYANOGEN (V).

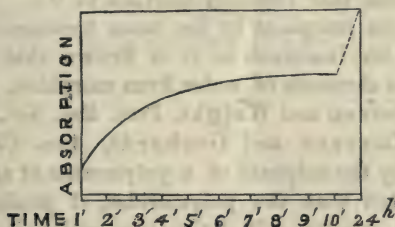
*Temperature per cent.*

	0°.	5°.	10°.	15°.	20°.	25°.	30°.	35°.	40°.	45°.	50°.	55°.	60°.	65°.	70°.	75°.
	114.3	112.4	110.0	108.4	106.4	104.4	104.0	100.2	98.2	96.4	94.7	94.3	91.7	90.2	88.3	86.7
	114.1	112.1	110.6	107.3	106.7	105.3	104.0	101.6	99.9	98.0	95.6	94.0	92.5	91.0	89.4	87.9
	112.8	110.5	109.3	108.4	106.0	104.7	103.7	100.8	99.3	97.6	94.6	94.6	—	88.8	87.0	85.5
	—	108.8	108.6	108.3	107.2	105.8	104.9	101.0	99.4	98.8	98.5	94.6	—	—	—	—
	—	—	—	108.6	107.8	105.9	—	102.0	98.4	97.9	—	—	—	—	—	—
	—	—	—	—	107.9	106.5	—	—	—	—	—	—	—	—	—	—
Average .....	113.7	110.9	109.6	108.2	107.0	105.3	103.7	101.1	99.2	97.8	96.2	94.4	92.1	90.0	88.2	86.7

the volume absorbed by one volume of cocat-nut charcoal as the temperature rises. In order to render the change in form of the curve more apparent, the vertical scale is drawn ten times as great as the horizontal.

In the tables on page 650, V is the volume of gas absorbed by one volume of cocoa-nut charcoal at the given temperature reduced to 760 mm.

It appears from a few observations on the time occupied by the absorption of cyanogen, that the process is almost entirely confined to the first ten minutes, and that afterwards it proceeds much more slowly. The accompanying table and curve illustrate the rapidity with which the absorption takes place, the time being measured on the horizontal, and the volumes on the vertical scale. V is the volume absorbed by one volume of cocoa-nut charcoal, corrected for pressure and temperature:—



Time .....	1'.	2'.	3'.	4'.	5'.	6'.	7'.	8'.	9'.	10'.	24 hrs.
V {	67.40	75.97	81.00	84.55	86.00	86.63	87.40	87.68	87.88	—	102.1
	68.18	74.14	76.95	78.58	79.41	80.23	81.06	81.85	82.46	83.06	107.27
	69.49	78.38	82.42	84.81	87.20	88.89	90.51	91.32	91.73	92.07	107.40
	56.35	68.83	76.80	78.45	80.18	82.00	83.70	85.00	86.40	87.40	107.10
	60.77	68.15	72.37	75.96	78.40	80.52	81.70	82.66	83.40	84.20	105.23
Average ....	63.61	73.09	77.91	80.29	82.24	83.65	84.87	85.70	86.37	86.68	105.82

Hydrogen and nitrogen are very slightly absorbed by cocoa-nut charcoal; one volume of the latter absorbs the following quantities, reduced to 3° C. and 760 mm:—

Hydrogen.	Nitrogen.
4.4	15.0
4.1	15.5
4.8	15.2
Average..	15.2



XXV.—*Action of Phosphoric Acid on Morphine.*

By C. R. A. WRIGHT, D. Sc. Lond., Lecturer on Chemistry in St. Mary's Hospital Medical School.

In a series of eight papers (the first three being in conjunction with the late A. Matthiessen) read before the Royal Society, a variety of new derivatives have been described, obtained from morphine and codeine by the action of various reagents, and in the last of these it has been shown that by the action of phosphoric and sulphuric acids on the latter of these two bases, polymerides are obtained containing probably twice, thrice, four times the number of symbols in their formulæ that are contained in the formulæ of the alkaloid itself (this formula being probably double that formerly ascribed to it). The production of similar bodies from morphine by the same treatment might, therefore, be expected; but inasmuch as it is known that sulphuric acid readily removes the elements of water from morphine, producing apomorphine (Matthiessen and Wright, *Proc. Roy. Soc.*, xvii, 455), and sulphomorphide (Laurent and Gerhardt, *Ann. Chim. Phys.* [3], xxiv, 112) (probably the sulphate of a polymeride of apomorphine), it might be anticipated that the polymerides, if produced, would be similarly converted into "apo"\* derivatives, which is found, in fact,

\* The prefix *apo* might be used with convenience to designate generally the removal of the elements of  $\text{H}_2\text{O}$ ; *diapo*, for the removal of  $2\text{H}_2\text{O}$ ; and so on. Thus:—

Ortho-sulphuric acid	$\text{S}(\text{OH})_6$	$= \text{SO}_3 + 3\text{H}_2\text{O}$	= Hydrated acid $\text{SO}_4\text{H}_2 + 2\text{aq.}$
Apo-sulphuric acid	$\text{SO}(\text{OH})_4$	$= \text{SO}_3 + 2\text{H}_2\text{O}$	= „ $\text{SO}_4\text{H}_2 + \text{aq.}$
Diapo-sulphuric acid	$\text{SO}_2(\text{OH})_2$	$= \text{SO}_3 + \text{H}_2\text{O}$	= Oil of vitriol.
Penta-disulphuric acid	$\text{S}_2\text{O}_5(\text{OH})_2$	$= 2\text{SO}_3 + \text{H}_2\text{O}$	= Nordhausen acid.
Triapo-sulphuric acid	$\text{SO}_3$		= Sulphur trioxide.

Similarly, the metallic salts of these acids may be conveniently designated—

Mercury orthosulphate	$\text{S}(\text{O}_2\text{Hg}'')_3$	= Turpeth mineral.
Copper orthosulphate	$\text{S}(\text{O}_2\text{Cu}'')_3$	= Tricupric sulphate.
Lead apo-sulphate	$\text{SO}(\text{O}_2\text{Pb}'')_2$	= Basic lead sulphate.
Potassium diapo-sulphate	$\text{SO}_2(\text{OK})_2$	= Ordinary neutral potassium sulphate.
Potassium-hydrogen diapo-sulphate	$\text{SO}_2(\text{OK})(\text{OH})$	= Acid potassium sulphate.
Potassium pentapo-disulphate	$\text{S}_2\text{O}_5(\text{OK})_2$	= Anhydro-sulphate of potassium.

And generally—

$$n.\text{apo-x.sulphate of M'} \quad \text{S}_x\text{O}_n(\text{OM}')_{6x-2n}.$$

Similarly the borates:—

Orthoboric acid	$\text{B}(\text{OH})_3$
Ethyl ortho-borate	$\text{B}(\text{OEt})_3$

to be the case. The morphine employed in these experiments, like all the alkaloids used in the former portions of these researches, amounting in the aggregate to several pounds weight, was most liberally presented for the purpose by Messrs. Macfarlane and Co. of Edinburgh.

When one part of morphine is treated with phosphoric acid solution (3 glacial acid to 5 water), and the liquid gently boiled until the boiling-point rises to  $180^{\circ}$ — $190^{\circ}$ , a brown liquid is obtained, which, when diluted with water, gives an immediate amorphous precipitate with excess of sodium carbonate; the filtrate from this, if quickly separated, contains unchanged morphine, which gradually crystallises out on standing. This precipitate is purified by solution in hydrochloric acid, reprecipitation by sodium carbonate, and rapid filtration; ether extracts a very small quantity (less than 0.6 per cent.) of a base soluble in that menstruum; on agitation with hydrochloric acid, anhydrous crystals are obtained, which present all the appearances and reactions of the hydrochloride of apomorphine. Dried at  $100^{\circ}$ —

0.1007 grm. gave 0.2485  $\text{CO}_2$  and 0.058  $\text{H}_2\text{O}$ .

	Calculated.		Found.
$\text{C}_{68}$ .....	816	67.22	67.30
$\text{H}_{72}$ .....	72	5.93	6.39
$\text{N}_4$ .....	56	4.61	
$\text{O}_8$ .....	128	10.54	
$\text{Cl}_4$ .....	142	11.70	

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$\text{C}_{68}\text{H}_{68}\text{N}_4\text{O}_8.4\text{HCl}$	1214	100.00
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Sodium apo-borate	$\text{BO}(\text{ONa})$	= Neutral borate of sodium.
Potassium apo-diborate	$\text{B}_2\text{O}(\text{OK})_4$	= Bloxam's borate from fusion of $\text{B}_2\text{O}_3$ and $\text{KOH}$ .
Sodium triapo-tetraborate	$\text{B}_4\text{O}_3(\text{ONa})_6$	= Arfvedson's borate from fusion of borax with $\text{Na}_2\text{CO}_3$ .
Sodium pentapo-tetraborate	$\text{B}_4\text{O}_5(\text{ONa})_2$	= Fused borax.
Ethyl pentapo-tetraborate	$\text{B}_4\text{O}_5(\text{OEt})_2$	= Acid ethyl borate.

And generally—

n.apo-x.borate of  $\text{M}'$        $\text{B}_x\text{O}_n(\text{OM}')_{3x-2n}$ .

Or, again, the silicates:—

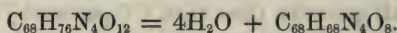
Orthosilicic acid       $\text{Si}(\text{OH})_4$   
 n.apo-x.silicate of  $\text{M}'$        $\text{Si}_x\text{O}_n(\text{OM}')_{4x-2n}$ .

Or, in many instances in organic chemistry—

Ortho-acetic acid	$\text{CH}_3.\text{C}(\text{OH})_3$	= Hydrated acid, $\text{C}_2\text{H}_4\text{O}_2 + \text{aq.}$
Lead ortho-acetate	$\text{CH}_3.\text{C}(\text{O}_2\text{Pb})_3\text{C}.\text{CH}_3$	= Tribasic lead acetate.
Apo-acetic acid	$\text{CH}_3.\text{CO}.\text{OH}$	= Glacial acid.
Potassium-hydrogen diapo-diacetate	$\text{CH}_3.\text{CO} \left\{ \begin{smallmatrix} \text{OH} \\ \text{OK} \end{smallmatrix} \right\} \text{CO}.\text{CH}_3$	= { Acid potassium salt.
Triapo-diacetic acid	$\text{CH}_3.\text{CO}.\text{O}.\text{CO}.\text{CH}_3$	= Aceticanhydride.

This product gave the apomorphine reactions with  $\text{Fe}_2\text{Cl}_6$ ,  $\text{NO}_3\text{H}$ , and  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{SO}_4\text{H}_2$ ; a dose of 0.005 gram given to a cat by subcutaneous injection, did not produce vomiting, but caused profuse salivation and considerable excitement, precisely analogous to the effects of the same dose of genuine apomorphine given to the same cat some days afterwards, when it had entirely recovered from the effects of the first dose.

From comparison of the results of the action of phosphoric and sulphuric acids on codeine and morphine, the conclusion is drawn that apomorphine has a much higher formula than that originally attributed to it, inasmuch as it is in all probability derived by dehydration from the dimorphine first formed by the reaction—



The results obtained by a closer study of the action of hydrochloric acid on morphine appear, as will be shown in a subsequent communication, to corroborate this view; comparison of the physical properties of apomorphine, and its salts, with those of the different codeine polymerides, likewise indicates a greater analogy to dicodeine than to ordinary or to tetra-codeine.

The portion of the precipitate produced by sodium carbonate, which is insoluble in ether, oxidises by exposure to air with great rapidity; dissolved in hydrochloric acid, and fractionally precipitated by sodium carbonate, it finally yields a light fawn-coloured precipitate, which rapidly darkens and absorbs oxygen while drying. Washed and dried as rapidly as possible, it gave the following numbers:—

0.325 grm. gave 0.7665  $\text{CO}_2$  and 0.172  $\text{H}_2\text{O}$ .

	Calculated.		Found.
$\text{C}_{136}$ .....	1632	64.46	64.32
$\text{H}_{148}$ .....	148	5.84	5.88
$\text{N}_8$ .....	112	4.42	
$\text{O}_{40}$ .....	640	25.28	
<hr/>			
$\text{C}_{136}\text{H}_{148}\text{N}_8\text{O}_{22} + \text{O}_{18}$	2532	100.00	

Converted into hydrochloride by moistening with hydrochloric acid, and evaporating to dryness, this oxidised base gave the following numbers:—

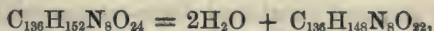
0.293 gave 0.119  $\text{AgCl}$ .

0.2865 „ 0.612  $\text{CO}_2$  and 0.145  $\text{H}_2\text{O}$ .



	Calculated.		Found.
C <sub>136</sub> .....	1632	57·80	58·24
H <sub>156</sub> .....	156	5·52	5·62
N <sub>8</sub> .....	112	3·97	
O <sub>40</sub> .....	640	22·66	
Cl <sub>8</sub> .....	284	10·05	10·06
<hr/>			
C <sub>136</sub> H <sub>156</sub> N <sub>8</sub> O <sub>22</sub> ·8HCl + O <sub>18</sub>	2824	100·00	

From these numbers it appears probable that the insoluble base is derived from tetramorphine by dehydration, in accordance with the reaction—



and this conclusion is strengthened by the results described in the next two sections; provisionally, therefore, this base may be termed *diapo-tetramorphine*, in accordance with the system of nomenclature hitherto employed.

## §2. Action of Hydrochloric Acid on Diapo-tetramorphine.

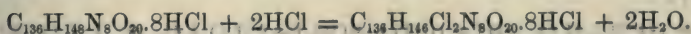
When freshly prepared diapo-tetramorphine (unoxidised) is dissolved in a large excess of strong warm hydrochloric acid, the solution boiled down gently almost to dryness, and finally evaporated to dryness on the water-bath, a tarry residue is obtained, readily soluble in water; addition of strong hydrochloric acid to this aqueous solution throws down flakes of the hydrochloride of a new base; this is obtained purest by fractional precipitation with strong hydrochloric acid, the last precipitate being washed with weak acid, and dried at 100°; a brownish, tarry, brittle mass is thus obtained, much resembling the hydrochloride of chloro-tetra-morphine,

0·318 gramm. gave 0·7415 CO<sub>2</sub> and 0·179 H<sub>2</sub>O.

0·236       ,,       0·1255 AgCl.

	Calculated.		Found.
C <sub>136</sub> .....	1632	63·43	63·59
H <sub>154</sub> .....	154	5·99	6·25
N <sub>8</sub> .....	112	4·35	
O <sub>20</sub> .....	320	12·44	
Cl <sub>10</sub> .....	355	13·79	13·16
<hr/>			
C <sub>136</sub> H <sub>146</sub> Cl <sub>2</sub> N <sub>8</sub> O <sub>20</sub> ·8HCl	2573	100·00	

Apparently, therefore, this compound is formed by the reaction—



In physical and chemical properties this substance much resembles chlorotetramorphine, from which it differs in formula by  $-H_4O_4$  (the formula of chlorotetramorphine being taken as  $C_{136}H_{180}Cl_2N_8O_{24}$ , or double that assigned to it at first); sodium carbonate throws down from its aqueous solutions fawn-coloured flakes, almost wholly insoluble in ether, and darkening by exposure to air; like all the other "tetra" bases it yields a blood-red colour on warming with an acid solution of silver nitrate.

### §3. Action of Hydriodic Acid and Phosphorus on Diapo-tetramorphine.

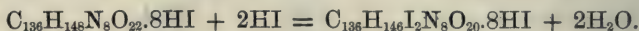
When freshly prepared unoxidised diapo-tetramorphine is dissolved in dilute hydriodic acid by the aid of heat, and the solution gently boiled down with the addition of excess of hydriodic acid and a piece of phosphorus, until the boiling-point rises to  $125^\circ$ , a viscid liquid is obtained, from which, on filtration through asbestos and precipitation by water, a substance is obtainable indistinguishable in appearance from the similar body obtained by the analogous treatment of tetracodeine. Dried at  $100^\circ$  it yielded the following numbers:—

0.346 grm. gave 0.577  $CO_2$  and 0.147  $H_2O$ .

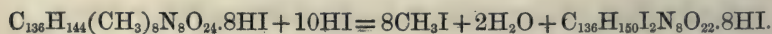
0.3565     ,,     0.242 AgI.

	Calculated.		Found.
$C_{136}$ .....	1632	46.79	45.48
$H_{164}$ .....	154	4.42	4.72
$N_8$ .....	112	36.41	36.68
$O_{20}$ .....	320	3.21	
$H_{10}$ .....	1270	9.17	
<hr/>			
$C_{136}H_{146}I_2N_8O_{20} \cdot 8HI$	3488	100.00	

This substance when heated yields a most difficultly combustible carbon, which accounts for the slight deficiency in the carbon determination. With nitric acid and silver nitrate it yields a blood-red colour, and not a yellow one, which, together with the analytical numbers, shows that no hydrogen has been taken up. Hence this substance is produced by the reaction—



which is perfectly parallel with the reaction with hydrochloric acid described in the last section, and with the action of hydriodic acid and phosphorus on tetracodeine (methyl being eliminated in the latter case):



From the foregoing results it appears that the action of phosphoric acid on morphine is analogous to that on codeine, in that polymerisation is brought about, with the difference that the elements of water are abstracted in the first case from the products, and not in the latter case. Diapo-tetramorphine resembles tetracodeine in its behaviour with hydriodic acid and phosphorus, in that the elements of hydriodic acid are added on and those of water removed (equivalent to a replacement of OH by I), but differs in that hydrochloric acid produces an analogous reaction, whereas tetracodeine is unaffected by this agent.

Dr. Reginald Stocker has examined the physiological action of diapo-tetramorphine on dogs, and finds that it is quite as energetic an emetic as apomorphine, if not more so; it does not, however, seem to produce quite so much after-depression; no difference in the result was observed whether 1, 5, or 10 centigrams of the hydrochloride had been subcutaneously injected, profuse vomiting being in each case induced in not more than five minutes. In one experiment 10 centigrams were injected into a healthy terrier which was suckling puppies of three weeks' age; profuse vomiting was produced in the mother, but no appreciable result was noticed in the puppies, although they were suckled by the mother a few minutes after the injection, and while the emetic action was still strongly marked. The preparation of diapo-tetramorphine is not difficult, and is not necessarily accompanied by the exhibition of its peculiar effects on the operator, a contingency difficult to avoid when the ether extraction process for apomorphine is employed on anything like a moderately large laboratory scale, but it has the disadvantage of not forming so slightly a preparation, its hydrochloride being only obtainable in the form of a more or less brown-black hygroscopic powder or gummy mass.

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#### XXVI.—*On Chinoline and Leucoline.*

By C. GREVILLE WILLIAMS, F.R.S.

IN the April number of the Journal of the Society, there is an abstract of a paper by M. Ballo, "On Leucoline Oil, and the Pure Naphthalene of Commerce." In that paper the author states that he obtained a copious yellow precipitate by heating the sulphate of leucoline with chromate of potassium. He also states that by acting on leucoline with iodide of amyl, and boiling the product with solution of hydrate of potassium, he obtains a violet colour, apparently identical with chinoline blue.

These experiments of M. Ballo seem to me to throw a light upon a



very difficult question, namely, the cause of the great discrepancy between the results of the chemists who have examined different specimens of leucoline. Hofmann, in his admirable paper on the coal-naphtha bases, states that at the commencement of his investigation of leucoline, he considered it to be identical with chinoline. The radical difference in their behaviour with a solution of chromic acid, however, soon convinced him that they were distinct. Subsequently (*Chem. Gaz.*, vol. iii, p. 251), Liebig announced that Hofmann had obtained with perfectly pure leucoline the characteristic crystalline precipitate with chromic acid. Fully aware of these results, I made a careful comparison of the action of chromic acid on chinoline and lepidine, on the one hand, and on leucoline and its next homologue, now called iridoline, on the other.\* The results showed chinoline and leucoline to have distinct properties. Chinoline and lepidine yielding with chromic acid crystalline salts of great beauty, giving on analysis almost theoretical numbers, while leucoline, even when recovered from a pure platinum salt which had been analysed, only gave a yellow oily precipitate.

With regard to the formation of chinoline-blue from leucoline, I have repeated my comparative experiments upon a small portion of leucoline remaining from my old investigation, and a fresh preparation of chinoline. The results were precisely the same as before. The chinoline gave at once and without difficulty the brilliant and characteristic reaction; the leucoline yielded a faint, dirty, purplish coloration, having no resemblance whatever to chinoline-blue.

The diversity in the results of the chemists who have examined this subject, is not difficult of explanation, if, as I believe probable, coal-tar sometimes contains chinoline as well as leucoline. There is no reason why such should not be the case, and the apparent contradictions would at once disappear.

M. Ballo's results are so interesting to me, that I propose to re-examine leucoline from various sources as soon as I can obtain a supply, and, whether the results are in harmony with my old ones, or are similar to M. Ballo's, I shall at once bring them before the notice of the Society.

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\* "On the Volatile Bases produced by Destructive Distillation of Cinchonine," *Trans. Roy. Soc. Edin.*, Vol. xxi, Part II, 1855. "Researches on Chinoline and its Homologues," *Trans. Roy. Soc. Edin.*, Vol. xxi, Part III, 1856.

XXVII.—*Note on a Secondary Colouring Matter produced in the Preparation of Alizarin from Anthracene.*

By W. H. PERKIN, F.R.S.

IN a paper on Artificial Alizarin, published in the Journal of this Society,\* I mentioned that there was produced, along with that colouring matter, a certain quantity of a second colouring matter, dyeing mordants very similarly to alizarin, with the difference that the purples were blue and the reds more scarlet.

I have since been examining this body, which is difficult to obtain pure. From numerous combustions it appears to have the formula—



The following is a comparison of the theoretical numbers, with the mean of four carbon and hydrogen determinations:—

$\text{C}_{10}$ .....	65·62	65·60
$\text{H}_8$ .....	3·12	3·22
$\text{O}_5$ .....	21·26	—

The colouring matter is difficultly soluble in most solvents. It crystallises from glacial acetic acid in groups of minute crystals of a yellow colour.

Up to the present time I have not succeeded in obtaining any very definite salts to control the foregoing results.

This formula is the same as that usually assigned to purpurin. The substance is, however, entirely different in properties from that colouring matter; for example, its ethereal solution does not give the characteristic bands when examined with the spectroscope, nor does it form the pink fluorescent solution when boiled with a solution of alum. It also dissolves in alkalis with a violet colour, not a red.

It also differs from alizarin in many ways. Its solution in caustic potash is not of such a blue violet, although it gives two bands when viewed with the prism, similar to those of alizarin, but not so marked. It dissolves in ammonia with a red-purple colour, and this solution gives no bands, whereas alizarin dissolves with a blue-violet colour, and gives two bands. Its ammoniacal solution, when added to aluminate of potash, produces no precipitate; an ammoniacal solution of alizarin gives a red lake, usually at once, but always after standing for some time.

This colouring matter is, therefore, distinct, both from alizarin and

\* Vol. xxiii, p. 143.

from purpurin; this is also seen from the colours produced upon mordants. I hope soon to be able to lay before the Society a more detailed account of this interesting body.

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XXVIII.—*On a remarkable Salt deposited from the Mother-Liquors obtained in the Manufacture of Soda.*

By T. E. THORPE, Ph.D., F.R.S.E., Professor of Chemistry in the Andersonian University of Glasgow.

IN a paper recently read before the Glasgow Philosophical Society (*Chem. News*, vol. xxv, 55), Mr. Mactear, of the St. Rollox Chemical Works, drew attention to the formation of fine ruby-coloured octohedral crystals in the highly concentrated mother-liquors obtained in the manufacture of soda by Leblanc's process. The occurrence of these crystals has been already observed. Rammelsberg (*Jahresbericht. f. Chem.*, 1864, 185) found for them the composition  $\text{Na}_3\text{PO}_4 + 10\text{H}_2\text{O}$ , and attributed their colour to the presence of a small quantity of vanadic acid. Baumgarten (*Jahresbericht.*, 1865, 219) however, has shown that this salt has in reality a more complicated composition; it invariably contains fluorine, and must be regarded as a double salt of trisodium phosphate and sodium fluoride. It would stand, therefore, to trisodium phosphate in a relation similar to that in which fluorapatite stands to tricalcium phosphate.

Mr. Mactear kindly furnished me with some specimens of these crystals for analysis. They were unusually large, being several centimeters in diameter; although their edges were considerably abraded, the octohedral habitus of the crystals was perfectly distinct. On treating them with cold water, they left a small quantity (1.74 per cent.) of insoluble matter, consisting of sulphide (sulphur, 0.3 per cent.) and phosphate of iron, and the solution became blue, or greenish blue. This coloration disappeared on standing, and on filtration a colourless solution was obtained, from which by evaporation colourless and perfectly regular octahedrons were obtained. These crystals consisted essentially of trisodium phosphate, containing small quantities of fluorine and vanadic acid, and traces of arsenic acid and silica. On standing in contact with the air, the solution absorbed carbonic acid, and ordinary rhombic phosphate of sodium was deposited.

The octohedral crystals were analysed with the following results:—  
1.8995 grm. lost at  $130^\circ$ , 0.8783 grm. water, = 46.2 per cent. On gentle ignition, 0.9230 grm., or 48.60 per cent. water was given off.



The residue on solution in water gave, after addition of silver nitrate, 2.265 grams of mixed phosphate and vanadate of silver.

The vanadic acid was estimated in the original substance by titrating with a dilute potassium permanganate solution. Two experiments were made. No. 1 gave 0.74 per cent.; No. 2, 0.71 per cent.  $\text{VO}_4$ . After removal of the excess of silver, the sodium was estimated as sulphate. Wt. of  $\text{Na}_2\text{SO}_4 = 1.3195$ . These numbers agree perfectly with those required by the formula proposed by Baumgarten, viz.,  $2\text{Na}_3\text{PO}_4 + \text{NaF} + 19\text{H}_2\text{O}$ , as the following comparison shows:—

	Found.	Calculated.
Water.....	48.60	48.01
Phosphoric acid ( $\text{PO}_4$ )....	26.02	26.67
Vanadic acid .....	0.73	—
Arsenic acid .....	traces	—
Sodium .....	22.52	22.63
Fluorine .....	—	2.69
		<hr/> 100.00

Baumgarten attributes the red colour of the original crystals to sulphide of iron; the colouring matter, whatever it may be, is very irregularly distributed throughout the crystals.

# ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

## Physical Chemistry.

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**On the Electromotive Force Developed by the Contact of Metals and Inactive Liquids.** By J. M. GAUGAIN (*Compt. rend.*, lxxiv, 610—613).

If two plates of platinum, the surfaces of which have been polished with emery paper, are allowed to remain in distilled water for 48 hours, no electric current is generated when the two plates are brought into metallic connection through a delicate galvanometer. If, however, one of the plates be taken from the liquid, and its surface rubbed with any soft substance, it is found, when plunged again into the distilled water, to be negative to the plate which has remained in the water. When the surface is rubbed with "papier Joseph," a force of 30 units is developed, during friction with linen moistened with water 40 units are developed; and if the plate be rubbed with wet linen for some time, and then with dry linen, the force rises to 56 units. The unit of force which serves as a measure is the electromotive force of a thermo-electric couple  $\left(\frac{\text{Bi} - \text{Cu}}{0^\circ - 100^\circ}\right)$ . The above values are given for the force

developed when the plate is plunged into distilled water immediately after rubbing; if, however, the plate after rubbing be allowed to remain either in dry or in damp air for some time, the force generated on immersion gradually decreases. The current generated diminishes very quickly after the plate has been immersed for a short time; after 10 minutes it diminishes to about one-half, but it is some hours before the two plates become perfectly neutral to each other. The cause of these currents may be that after rubbing the plate does not immediately become thoroughly moistened by the water, for if it be taken out of the water, the liquid on the surface will be seen to run together into drops. The plate, however, recovers its power of being thoroughly moistened if it be heated in a spirit-lamp flame. It seems as if the rubbing caused a small film of grease to be deposited on the surface, which is destroyed by heat. Becquerel has found that if two plates of platinum are taken, and, after remaining in distilled water for some time, one of them be taken out and exposed to the air, this plate on immersion is negative to the one which had remained in the water. The force generated, however, never rises to more than 5 or 6 units, and therefore the rubbing in the former cases must have contributed the greater part to the development of the electromotive force.

A. P.

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**On the Electromotive Forces Developed by the Contact of Metals and Inactive Liquids.** By J. M. GAUGAIN (Compt. rend., lxxiv, 1332).

A PLATINUM plate, which has been exposed to heat without previous friction with linen, is, when immersed in water, electronegative towards a normal platinum plate *already* immersed, the electrical difference being greater when the heating has been performed in the flame than when in a closed vessel.

In these experiments the plate is supposed to be immersed in water immediately after cooling; when, before the plate immersion, is left exposed to the air for one or two days it is found to be less electronegative, the loss of electromotive force increasing with the amount of moisture in the air.

Becquerel ascribes the negative electric condition exhibited by platinum on immersion in water to the gradual detachment of the oxygen which had been absorbed by the plate during its contact with air, whilst in Germany the opinion is prevalent that the platinum absorbs oxygen whilst immersed in water.

These two opinions being quite contradictory to each other, inasmuch as absorption of oxygen would, according to the first, render the plate less positive, and, according to the second, more positive, are not considered satisfactory by the author, who attributes the electrical difference between the two plates, immersed in water, to their being endowed in different degrees with that affinity which causes water to adhere to platinum. This affinity he believes to be diminished by rubbing with linen, because from experiments described in the first part of his communication (see last abstract) platinum appears after this operation to be less easily wetted by water.

That the plate becomes electronegative by temporary exposure to heat is probably caused by the removal of the film of moisture adhering to the surface.

From this it also follows that a platinum plate rendered electronegative by rubbing with linen can by temporary exposure to heat be restored partly, but not completely, to its normal condition, inasmuch as only the hardening of the surface, which is produced by friction and causes a certain proportion of the (negative) electrical tension, will be destroyed by heat.

R. S.

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**Effect of the Non-luminous Discharge.** By BERTHELOT (Compt. rend., lxxiv, 1462).

BABO'S ozone apparatus, with a sparkless discharge, gives only faint traces of acetylene, while Houzeau's instrument, with small but just visible sparks, furnishes a more considerable quantity. In the luminous discharge the temperature is higher, and therefore more favourable for the production of acetylene, &c., though not for that of ozone. Thus Thénard has found that carbon dioxide is decomposed very slowly by Babo's, less slowly by Houzeau's apparatus, but very rapidly by brilliant sparks.

C. G. S.



*Report to the "Comité de Chimie et de Physique de l'Ecole Polytechnique" on a Proposed Modification of Bunsen's Battery.* By F. LEBLANC (Ann. Chim. Phys. [4], xxv, 289—322).

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*Observations on the Two-liquid Battery, and on the Modifications which may give rise to Variations in the Energy of Bunsen's Battery.* By F. LEBLANC (Ann. Chim. Phys. [4], xxv, 323—334).

THIS is the full paper of which an abstract from the *Comptes rendus* has already been given in this Journal (1871, p. 1133).

*Remarks on the Preceding*, by E. BECQUEREL (Ann. Chim. Phys. [2], xxv, 138), who points out that the principle of two-liquid batteries, and of constant batteries in general, was first demonstrated by his father in 1829 (*ibid.* [2], xli, 21 and 293).

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**Influence of Pressure on the Lines of the Spectrum.** By L. CAILLETET (Compt. rend., lxxiv, 1282).

WHEN the spark of an induction coil excited by three Bunsen's elements was passed between platinum electrodes at 2 or 3 millimeters distance through air contained in a tube of very thin glass, the light of the discharge was very feeble, and gave a spectrum of distinct lines on a nearly dark ground. On increasing the pressure, the lines gained gradually in brightness, and widened out, until at last the spectrum became continuous, and the individual lines could no longer be distinguished. An increase of pressure beyond this point put a sudden stop to the discharge, and all the author's attempts to prevent this sudden extinction, which takes place at a pressure of about 40 to 50 atmospheres, failed.

In the case of hydrogen it was especially the red ray  $\alpha$  which gained in brightness, until at a pressure of nearly 40 atmospheres the red portion of the spectrum became so luminous, that this ray was difficult to recognise, whilst at the same point the ray  $\gamma$  was already completely blended with the more refrangible portion. Also with the other gases examined, air and nitrogen, the less prominent lines became totally indiscernible before the cessation of the luminous discharge. Sometimes the glass was attacked, and then the sodium lines appeared with great intensity.

When the electrodes had been dipped in solutions of sodium, lithium, or thallium, it was found that the characteristic rays of these metals not only became more intense by increasing the pressure of the gas contained in the tube, but that they remained distinct, even when the gaseous spectra had already vanished, and the metallic spectra had become nearly continuous. The author believes that if observations were possible at still higher pressures, continuous metallic spectra might be obtained.

The intensity of the luminous spark at a pressure of 40 atmospheres is about 200 times greater than at the pressure of 1 atmosphere.

R. S.

**Absorption Spectra of the Vapours of Selenium, Selenious Chloride and Bromide, of Tellurium, Tellurous Chloride and Bromide, of Iodine Bromide, and of Alizarin.** By D. GERNEZ (Compt. rend., lxxiv, 1190—1192).

If selenium be heated in a porcelain tube by a series of gas-jets whilst a ray of white light is passed through the tube, the spectrum will be found to be gradually extinguished from the violet up to the red, without any appearance of black lines; on raising the temperature considerably, the spectrum becomes brighter, and bundles of black lines appear furrowing the blue and violet. This spectrum resembles that of selenious anhydride, but the above spectrum was obtained in an atmosphere of dry carbonic anhydride, so that selenious anhydride could not be produced.

Selenious chloride vapour gives an absorption-spectrum of lines which extend from the green to the violet.

Selenious bromide vapour produces a system of lines almost equidistant, when observed in a thickness of 10 centimeters.

Tellurium, when heated nearly to the melting-point of glass, gives off a golden-yellow vapour, which gives a spectrum consisting of fine lines stretching from the yellow to the violet.

Tellurous chloride vapour, one centimeter in thickness, produces a spectrum particularly developed in the orange and green.

Tellurous bromide gives a violet vapour, the more pronounced lines of which are in the red and yellow.

Bromide of iodine vapour in a tube 80 centimeters long, gives a number of very fine lines in the red, yellow, and orange. This spectrum differs from the combined absorption-spectra of bromine and iodine.

Alizarin cautiously heated gives off vapours, which produce systems of lines sensibly equidistant in the mean region of the spectrum.

A. P.

**Relations between the Optical Rotatory Powers of Organic Bodies.** By F. W. KRECKE (Archives Néerlandaises, vi, 1871, and J. pr. Chem. [2] v, 6—23).

THE author has determined the "specific molecular rotatory power" of many organic substances. The formula used by Biot for the calculation of this number he does not regard as correct, as it gives the specific rotatory, but not the specific *molecular* rotatory power.

Biot's numbers are given by the formula—

$$[\alpha] = \frac{\alpha}{\epsilon l \delta}$$

$\alpha$  = observed angle of rotation for a particular tint.

$\epsilon$  = quantity of active substance in unit-length of the solution.

$l$  = length of the column.

$\delta$  = density of solution.

To calculate the specific molecular rotatory power,  $= [m]$ , the author employs the formula—

$$[m] = \frac{\alpha \cdot w}{\epsilon \cdot l \cdot \delta \cdot 100}$$

$w$  being the molecular weight of the given substance.

The introduction of the factor 100 into the denominator is equivalent to taking the millimeter for the unit of length instead of the decimeter, as in Biot's formula.

The author has determined the value of  $[m]$  for many classes of organic bodies, viz., glucosides, hydrocarbons, camphors, acids, alcohols, alkaloids, &c. For glucose and allied substances,  $[m] = 48.5$ , taking the mean of a number of determination. For saccharoids (lactose, &c.),  $[m] = 24.96$ , alkaloids, &c.

These experiments lead to the two following laws:—

(1.) When an optically active substance combines with one optically inactive, or is modified by chemical agency, its specific molecular rotatory power either remains unchanged, or is so modified that the number now expressing it is a simple multiple of the former number.

(2.) The numbers expressing the specific molecular rotatory powers of isomeric substances are multiples of one and the same number.

These laws the author applies as follows:—

Racemic acid is made up of one molecule of dextro- and one molecule of lævo-tartaric acid. Suppose a compound of five molecules of dextro- with one molecule of lævo-tartaric acid; add another molecule of the dextro-acid; it will be neutralised by the molecule of the lævo-acid, and there will remain four molecules rotating the plane of polarisation to the right. This substance will possess, therefore, two-thirds the rotating power of dextro-tartaric acid.

If then we have a group of optically active substances, by choosing that which is most dextro-rotatory, and adding to it one which possesses an equal lævo-rotatory power, we can, by combination of different numbers of atoms of these two, form all the other members of the group.

M. M. P. M.

**Expansion of Moist Gases.** By M. AMAGAT (Compt. rend., lxxiv, 1299).

TAKING the coefficient of expansion of dry air,  $= .00367$ , and that of dry sulphur dioxide,  $= 0.00390$ , the author finds that the coefficient of expansion of air which has not been dried, or which has passed through a wash-bottle containing water, lies between  $0.00368$  and  $0.00369$ , and that of moist sulphur dioxide between  $0.00395$  and  $0.00396$ . He concludes from this (1) that the influence of moisture upon



the dilatation of gases is by no means so great as is supposed by some physicists, who attribute the differences between the coefficients of expansion of different gases to the presence of moisture; (2) that it is impossible to determine the quantity of watery vapour in the air by its influence upon the coefficient of expansion.

R. S.

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**An Experiment relative to the question of Vesicular Vapour.**

By J. PLATEAU (*Ann. Chim. Phys.* [4] xxv, 284—288).

WHEN a tube with small orifice is filled with water and inverted, the water, as is well known, remains in the inverted tube. The author finds that if an air-bubble less than one millimeter in diameter is blown with water at the end of a small glass tube, and introduced at the surface of the suspended water, the air-bubble does not cause any disturbance, but simply rises into the tube. An inverted tube containing water can be suspended over a jet of steam for some time without bubbles of gas or any turbidity being produced in the tube. The author regards these experiments as constituting, if not a proof, at least as a strong argument against the "vesicular state."

If a soap bubble of about one centimeter is blown, and placed in an atmosphere saturated with aqueous vapour, at the end of twenty-four hours the film appears entirely black, after which time the soap-bubble begins to decrease gradually until it is lost, from which it appears that the contained air has slowly passed through the film of soap and water.

A. P.

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*Gas Thermo-regulator for High Temperatures.* By D. JEANNEL (*Ann. Chim. Phys.* [4], xxv, 386); also by MILNE-EDWARDS (*ibid.*, 390).

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**Inorganic Chemistry.**

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**Decomposition of Carbon Dioxide under the influence of the Electric Discharge.** By ARNOULD THÉNARD (*Compt. rend.*, lxxiv, 1280).

THE author, by passing a slow current of carbon dioxide through a tube similar to those used by Houzeau for the preparation of ozone, has found that from 4 to 8 per cent. of the gas is decomposed, and yields, after absorption of the remaining carbon dioxide by potassium hydrate, a mixture of 1 volume of carbon oxide and  $\frac{1}{2}$  volume of oxygen, of which 265 c.c. were obtained in 30 hours. Its action upon potassium iodide and upon indigo solution proved that some ozone had been formed, although its quantity was too small to be determined. From

these observations it appears probable that the energy of the discharge is almost exclusively consumed in breaking up the carbon dioxide. The author proposes to extend these experiments to other gases.

R. S.

**Daily Observations at Rostock on the amount of Carbon Dioxide in the Atmosphere.** By F. SCHULZE (Versuchs-Stationen Organ., xiv, 366—389).

THE following table gives the means for each month, during the duration of the experiments, of the parts by volume of carbon dioxide found in 10,000 parts of air.

1868.	1869.	1870.	1871.
October .. 3·0600	January .. 2·7297	January .. 2·9866	January .. 2·9727
November . 2·9040	February . 2·9214	February . 2·7621	February . 3·0135
December . 2·7191	March.... 3·0487	March.... 2·8419	March ... 3·0888
	April .... 3·0973	April .... 2·8247	April .... 2·9813
Mean .. 2·8943	May .... 2·8480	May .... 2·8595	May .... 3·1191
	June .... 2·8960	June .... 2·8910	June .... 2·9777
	July .... 2·8087	July .... 2·9368	July .... 2·9361
	August .. 2·8500	August .. 2·8985	
	September 2·8347	September 2·9720	Mean .. 3·0126
	October .. 2·7964	October .. 2·9835	
	November. 2·7653	November 2·9096	
	December. 2·8008	December. 2·9976	
	Mean .. 2·8668	Mean .. 2·9052	
Total mean, 2·9197.      Maximum quantity, 3·44.      Minimum, 2·25.			

During the latter period of the experiments the carbon dioxide was determined twice in the day, by shaking a standard solution of barium hydrate with 4 litres of air, and titrating with oxalic acid, tincture of turmeric being used as an indicator. The results by this method agreed closely with those obtained by passing 25 litres of air through baryta-solution by means of an aspirator.

The lowness of the results may be due to the vicinity of Rostock to the sea, as they most nearly agree with those obtained by Thorpe in the air over the Irish Sea and Atlantic Ocean.

No definite change in the amount of carbon dioxide was observed at different seasons of the year, or at different times of the day. Fog, and also a fall of snow, were often associated with an increase in carbon dioxide. The action of rain is not so obvious, and the changes are probably more dependent on the wind and temperature at the time, and on the action of the moistened soil, whether forming and liberating carbon dioxide or absorbing it. A north-east wind from the continent was found to increase the carbon dioxide, and a south-west wind to decrease it, probably owing to absorption by the sea. Distilled water shaken up with air was found to dissolve as a mean·83 milligrams of carbon dioxide per litre; fresh fallen rain-water contained 1·073 milligram per

litre. Water from the Baltic gave on boiling 11·83 milligrams of carbon dioxide per litre; by passing hydrogen through the water a somewhat smaller quantity was obtained. In the latter case the same quantity of carbon dioxide that had been obtained from the water was reabsorbed on shaking it up with air, but the sea-water, which had been boiled, redissolved only  $\frac{1}{3}$  to  $\frac{1}{4}$  the quantity, leading to the inference that the magnesium chloride and calcium and magnesium carbonates have an action in the solution of carbon dioxide by sea-water.

E. K.

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**Some Reactions of Pyrosulphuric Acid.** By E. DRECHSEL (J. pr. Chem. [2], v, 367).

THE author brings forward the following experiments as proofs that sulphuric and pyrosulphuric acids are really distinct compounds.

If finely powdered potassium pyrosulphate—prepared by heating fused hydrogen-potassium sulphate to dull redness—be boiled for some time with an alcoholic solution of potassium sulphhydrate, the residue contains considerable quantities of thiosulphate.

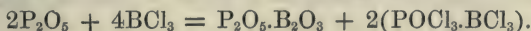
On boiling potassium pyrosulphate with an alcoholic solution of sodium ethylate, potassium sulphovinate is produced.

H. E. A.

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**Action of Phosphoric Oxychloride on Boric Anhydride.** By G. GUSTAVSON (Deut. Chem. Ges. Ber., iv, 975—976).

WHEN boric anhydride is heated with phosphoric oxychloride in closed tubes, to 150°—170°, for eight or ten hours, a white mass,  $P_2O_5.B_2O_3$ , is formed, whilst colourless crystals of a compound,  $POCl_3.BCl_3$  sublime in the upper part of the tube. The latter melts in a closed tube at 73°, and when sublimed splits up into boric chloride and phosphoric oxychloride. Crystals of the new compound are also formed on passing the vapours of boric chloride into phosphoric oxychloride, and by heating boric chloride with phosphoric anhydride to 200° for two or three days, the reaction being—



It is decomposed in contact with water, or by the moisture of the atmosphere, phosphoric acid, boric acid, and hydrochloric acid being formed. The white mass  $P_2O_5.B_2O_3$  is probably a mixture of phosphoric with boric anhydride, as it is resolved by water into phosphoric acid and boric acid, but if previously heated to redness it forms the compound  $B_2O_3.P_2O_5 = PBO_4$ , described by Vogel (*Zeitschr. f. Chem.*, 1870, 125), which is insoluble in water. From the readiness with which boric chloride combines with phosphoric oxychloride, the author considers that boron should be classed in the same group as aluminium.

C. E. G.



**Molecular Combinations of Phosphoric Bromochloride with Bromine.** By A. MICHAELIS (*Deut. Chem. Ges. Ber.*, v, 411—417).

THE author refers to his former researches on phosphorus bromochloride,  $\text{PCl}_3\text{Br}_2$  (*Deut. Chem. Ges. Ber.*, v, 970; p. 282 of this volume). This compound, a solid crystalline substance, is formed by bringing together phosphorous chloride and bromine in a glass tube, and exposing this for several days to the winter's cold; the excess of phosphorous chloride is then drained off from the crystals of  $\text{PCl}_3\text{Br}_2$ . This excess of phosphorous chloride forms with bromine a new compound.

The substance  $\text{PCl}_3\text{Br}_2$ , heated to  $35^\circ$ , is resolved into two liquid layers, the lower being dark, the upper lighter in colour; if a crystal of  $\text{PCl}_3\text{Br}_2$  be now dropped into this lower layer, crystallisation sets in throughout the liquid, and a substance is obtained (the same as that obtained by addition of bromine to the excess of phosphorous chloride run off from the crystals of phosphoric bromochloride; see above), in dark-yellow crystals, which gave, on analysis, numbers corresponding to the formula  $\text{PCl}_3\text{Br}_4$ .

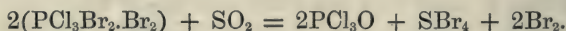
The compound was not changed by shaking it with excess of phosphorous chloride for twelve hours.

The dark liquid from which the  $\text{PCl}_3\text{Br}_4$  was obtained was shown by analysis to consist of 100 parts by weight  $\text{PCl}_3$ , and 299.8 parts Br; with these numbers the formula  $\text{PCl}_3\text{Br}_4$  agrees pretty closely.

The formation of  $\text{PCl}_3\text{Br}_4$  is accounted for by the author thus:—The dark liquid is a solution of  $\text{PCl}_3\text{Br}_2$  in bromine, and when a crystal of solid  $\text{PCl}_3\text{Br}_2$  is added to it, the phosphoric bromochloride combines with the excess of bromine, and crystallises with it, as many salts do which contain water of crystallisation.

This compound,  $\text{PCl}_3\text{Br}_4$ , forms large dark-red crystals, reflecting blue light; when heated they melt, forming two liquids, the original crystals being reproduced on cooling.

Towards sulphur dioxide,  $\text{PCl}_3\text{Br}_4$  behaves as a mixture of one molecule of  $\text{PCl}_3\text{Br}_2$  with one of bromine. The reaction is:—



By the action of a large excess of bromine on phosphorous chloride there is formed a solid substance, crystallising in brown needles, and having the formula  $\text{PCl}_3\text{Br}_8$ . This substance has been described by Prinvault (*Compt. rend.*, lxxiv, 868); but, according to the author, it is not liquid at  $4^\circ$ — $5^\circ$ , but melts only when heated to  $25^\circ$ ; nor has it the formula  $\text{PBr}_5.3\text{ClBr}$  assigned to it by Prinvault, because if this were its formula, it should be converted by sulphur dioxide into phosphoric oxybromide and bromine chloride; but the products actually obtained are phosphoric oxychloride and bromine sulphide; the compound should, therefore, be regarded as  $\text{PCl}_3\text{Br}_2.3\text{Br}_2$ .

As we have the molecular compounds  $\text{PCl}_5.\text{ICl}$ ,  $\text{PCl}_5.\text{FeCl}_3$ ,  $\text{PCl}_5.\text{SnCl}_4$ ,  $\text{POCl}_3.\text{BCl}_3$ , &c., so we have the molecular compounds  $\text{PCl}_3\text{Br}_2.\text{Br}_2$  and  $\text{PCl}_3\text{Br}_2.(\text{Br}_2)_3$ .

Lately a distinction between atomic and molecular compounds has

been based upon the ease or difficulty with which a given compound suffers or takes part in double decomposition. These new substances afford further examples of molecular compounds.

M. M. P. M..

### Separation of Crystalline Silicic Acid from Watery Solutions.

By O. MASCHKE (Pogg. Ann., cxlv, 549—578).

SOLUTIONS of amorphous silicic acid in caustic soda ( $\text{Na}_2\text{Si}_4\text{O}_9$ ) were heated in sealed glass tubes, placed inside iron tubes laid in powdered coal or sand in an Erlenmeyer's furnace, which was covered with a mantel of sheet iron.

Various little modifications and appliances are described by the author by which he was enabled to regulate the temperature, prevent explosions, &c.

50 c.c. of a solution containing 3.95 per cent. sodium were boiled in a platinum dish with amorphous silicic acid, allowed to cool under a bell jar, and with the clear liquid, after subsidence, manometer tubes, which were drawn out at the middle, were filled, and sealed at a pressure of 28 mm.

These tubes were heated to  $175^\circ$ — $185^\circ$  during 24 hours. The tubes were then no longer transparent, except the middle part which contained no liquid, where small crystals were easily visible. The tubes were opened, the liquid poured into a beaker, and the middle part of the tube cut off from the ends; both parts were dried and examined.

The liquid contained small grain-like particles; these washed with water, warmed with nitric acid (1.18 specific gravity), and again washed, appeared under the microscope to consist chiefly of peculiar tubercular (*knollenförmiger*) forms, interspersed with a few sharp-pointed crystals. The smaller of these crystals act feebly, the larger energetically on polarised light.

The middle parts of the tubes showed crystals, some gathered into groups, others scattered singly here and there; these behaved like those above described, and appeared to consist of hydrated silicic acid.

The end portions of the tubes were covered with a solid substance which, under the microscope, showed various kinds of laminae, fragments of glass, and a few of the peculiar tubercular crystals of silicic acid; by treatment with nitric acid, washing, digesting in caustic soda, and again washing, nothing remained but these tubercular crystals mixed with little pieces of glass.

By microscopic examination, by the action of light, by action of caustic soda, and by determination of specific gravity, the author has shown that these peculiarly-shaped crystals of silicic acid may be separated into two parts, an outer and an inner, the inner or kernel being identical with the mineral tridymite, as described by G. vom Rath, while the outer consists of small quartz crystals.

The author's experiments lead generally to these conclusions:—

The glass tube is attacked by the solution of sodium silicate. Silicic acid goes into solution, while a sodium silicate, comparatively richer in silicic acid, is formed, which, on cooling, changes into a compound

containing less silicic acid, the excess of this acid being deposited in tubercular crystals.

The influence of temperature upon the character of the precipitated silicic acid is that at about  $180^{\circ}$  C. free silicic acid is precipitated as quartz; below  $180^{\circ}$  first as tridymite, then as crystallised, and, lastly, as amorphous hydrated silicic acid.

The author thinks that increased pressure may effect considerable changes in the manner of precipitation of silicic acid, but that, under no circumstances, can quartz be precipitated from watery solutions at ordinary or slightly elevated temperatures, and under ordinary pressure.

M. M. P. M.

**A New Sodium Metasilicate.** By THEODOR PETERSEN  
(Deut. Chem. Ges. Ber., v, 409—410).

THE salt was obtained from a chemical work; a reddish sediment, rich in iron oxide, was noticed while evaporating down crude caustic soda liquor; this lixiviated with water, gave a solution, from which, when evaporated to  $37^{\circ}$  B., the new salt crystallised out. The crystals are colourless, transparent, becoming dim after standing in the air. They melt by gentle warming, and leave when ignited a white mass, very soluble in water. Analysis leads to the formula  $\text{Na}_2\text{OSiO}_2 + 5\text{H}_2\text{O}$ . The crystals belong to the monoclinic system, the ratio of the three axes being  $1.723771 : 1 : 1.4365492$ .

Four other sodium meta-silicates are known, containing respectively 9, 8, 7, and 6 atoms of crystalline water.

M. M. P. M.

**Solubility of Oxides in Alkali.** By PRUD'HOMME (Bull. Soc. Chem. de Paris, xvii, 253).

SOME oxides which are insoluble, or but slightly soluble, in an alkali, may be rendered soluble by the addition of an oxide which dissolves in that alkali. Thus, chromic oxide dissolves in ammonia when a salt of copper is added, and cupric oxide dissolves in potash if a salt of chromium be present.

B. J. G.

**Decomposition of Soluble Metallic Sulphides by Water.** By JULIUS THOMSEN (J. pr. Chem. [2], v, 247).

FULLY admitting that the decomposition of soluble sulphides of water is partial, and that it is more complete the greater the quantity of water present, the author is nevertheless of opinion, that in order to prove such a partial decomposition, some other method than the reaction of sodium sulphide and water on potassium sulphovinate employed by Kolbe (this Journal, x, 224), must be made use of, since in that case sodium sulphide, sulphhydrate, and hydrate all react at the same time, and it is impossible to draw a trustworthy conclusion as to



the simultaneous action of these three bodies on the sulphovinate from the yield of ethyl sulphide.

H. E. A.

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**Composition of the Precipitate Formed by adding a Solution of Ammonio-Sodic Phosphate to Solution of Calcium Chloride.** By J. W. C. DAVIS (Chem. News, xxv, 258).

It was noticed that when a cold solution of calcium chloride was added to a solution of microcosmic salt, a precipitate was formed which, though at first flocculent, became after a short time distinctly crystalline. The crystals, which were colourless and transparent, consisted of thin rhombic tables, with plane angles of  $30^\circ$  and  $150^\circ$  respectively; the acute angles being often truncated by short planes.

To ascertain the composition of this precipitate, it was divided into two portions, of which one was partially and the other completely washed with distilled water. Both specimens were then analysed. The percentage results obtained from the two preparations, though differing slightly *inter se*, calculated very closely to the formula of dicalcic orthophosphate with four molecules of water,  $\text{Ca}_2\text{H}_2\text{P}_2\text{O}_8 + 4\text{H}_2\text{O}$ .

This latter salt, although well known, and already described by Raewsky, Bödeker, and others, does not appear to have been previously prepared in a manner similar to that described by the author in the present paper.

J. W.

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**Experiments on Acid Sulphite of Magnesium.**

By R. H. DAVIES (Pharm. J. Trans. [3], ii, 965).

SOME discussion having lately taken place respecting the possibility of preparing acid sulphite of magnesium in a crystallised condition, the author undertook certain experiments in order to decide the question.

A solution of acid sulphite of magnesium was prepared and analysed in order to have satisfactory evidence respecting its composition.

A portion of the above solution was slowly evaporated by exposure to the air, and another portion by a gentle heat upon a water-bath; the crystals obtained in each case were carefully collected and examined. The crystals which were deposited at the normal temperature were found to consist wholly of magnesium sulphate, while those which had been obtained by the more rapid evaporation yielded analytical numbers exactly corresponding with those calculated from the formula of the neutral sulphite,  $\text{MgSO}_3 + 6\text{H}_2\text{O}$ .

Upon these grounds, the author considers that under ordinary conditions it is impossible to prepare acid sulphite of magnesium in a crystalline form. It is quite certain that the article known in commerce as "Bisulphite of Magnesia," is incorrectly so termed; the more so, as an examination of the salt showed it to consist mainly of the neutral sulphite.

J. W.

**Composition of the Crystalline Deposit from a Solution of Magnesium and Ammonium Chloride.** By J. W. C. DAVIS (Chem. News, xxv, 258).

THE author has examined the crystalline deposit which so frequently occurs in the laboratory reagent known as "magnesia mixture," when the latter has been allowed to remain undisturbed for some time.

It proved to be magnesium oxychloride, the mean results of three analyses leading to the formula  $\text{MgCl}_2 \cdot 5\text{MgO} + 13\text{H}_2\text{O}$ ; or as it may be also written,  $\text{Mg}_2\text{Cl}_2\text{O} \cdot \text{H}_2\text{O} + 4(\text{MgO} \cdot 3\text{H}_2\text{O})$ .

By washing the crystals with a large quantity of water, the whole of the chlorine can be removed and the oxychloride converted into hydrate. This hydrate was also examined, but the analytical results did not, in this case, establish any very definite formula. J. W.

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**Composition of the Deposit from Retorts in which Carbon Disulphide had been made.** By F. P. DUNNINGTON (Chem. News, xxv, 259).

A SPECIMEN of the compact deposit or crust which collects on the interior of cast iron retorts in which the manufacture of carbon disulphide is carried on, presented, in the present instance, the appearance of a nearly black mass, with traces of a bronze-yellow tint. It was 33 mm. in thickness, and divisible by the eye into three tolerably distinct layers of 6, 10, and 17 mm. respectively. The two thinner inferior layers were compact, granular in fracture, with an imperfect metallic lustre; the superior layer was less compact, but had a distinctly crystalline, slender prismatic structure, and decided metallic lustre.

All three were found to consist simply of sulphur and iron in chemical combination, the percentage of sulphur being—

1. In the layer in contact with the iron, 28·24 per cent.
2. In the median layer, 30·38 per cent.
3. In the superior layer, 38·10 per cent.

Nos. 1 and 2 contain an excess of iron over and above that required to form with the sulphur a monosulphide, but no separate grains or particles of iron could be detected. The carbon of the iron was completely removed. J. W.

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**Action of Oxygen on Copper Nitrate in a State of Tension.**

By J. H. GLADSTONE and ALFRED TRIBE (Proc. Roy. Soc., xx, 290).

THE authors, in their experiments on the action between copper and silver nitrate in solution, frequently noticed that the tips of the silver crystals became red, as though coated with a thin layer of metallic copper.

This apparent deposition of a positive on a more negative metal, led them to look closely into the circumstances under which it occurred. They found that it took place only when the silver nitrate was exhausted, and only on those crystals which remained in metallic connec-

tion with the copper; also that the cupreous coating formed most readily where air had the freest access, and in fact that it would not form at all in vessels from which oxygen was excluded, nor on those white crystals which were far below the surface of the liquid, though they might be in immediate contact with the copper plate. When an inverted jar was filled with solution of copper nitrate and silver crystals resting on branches of copper, and the liquid was displaced by oxygen gas, it was found that the tips of the crystals became red, and that the solution gradually filled the jar again by absorption of the gas. In the same way the oxygen was absorbed from air, or from its mixture with hydrogen or carbonic anhydride.

This action was further studied by employing plates of the two metals instead of copper covered with silver crystals. When the two plates, connected by a wire, were partially immersed in an ordinary aqueous solution of copper nitrate, it was found that a slight yellowish deposit made its appearance speedily all over the silver plate, and went on increasing for a day or two, while at the air-line there was a thicker deposit, which gradually grew and extended itself a little below the surface. This deposit changed from yellowish to red, and under the microscope presented a distinctly crystalline appearance.

Thinking that this slight crust all over the silver plate was due to air dissolved in the solution itself, they took advantage of the reaction to prepare copper nitrate free from dissolved oxygen. An ordinary solution of the salt mixed with some silver nitrate was placed in a narrow cylinder, with a long piece of copper-foil arranged somewhat spirally, so as to retain the deposited silver on its surface, and allowed to rest for twenty-four hours. The solution thus obtained was exposed to the action of the conjoined copper and silver plates; but even after some hours there was no dimming of the lustre of the silver plate, except at the air-line, which was sharply defined. The same solution, shaken for some time in the air, produced a yellowish deposit on the white metal in three minutes.

The colour and general appearance of this crust, together with its formation only where oxygen can be absorbed, showed that it was not metallic copper, but the suboxide. This was confirmed by the usual tests; also by a curious reaction, which requires a microscope to observe it properly. When treated with a solution of silver nitrate, this cupreous deposit does not give the ordinary crystals of the white metal; in fact, it is only slowly acted upon: but presently there shoot forth thin threads of silver, which run through the liquid, often twisting at sharp angles, while the yellowish crystals change to black. This was found to be a property of the suboxide of copper.

This deposition of oxide on the silver is accompanied by a corresponding solution of copper from the other plate. Thus in an experiment continued for four days with solution of copper nitrate which had been exposed to air, there was found—

Gain of silver plate, 0.016 grm.

Loss of copper plate, 0.015 grm.

The copper necessary for the production of 0.016 grm. of suboxide would be a little above 0.014 grm.



If the two plates have their sides parallel, the suboxide is deposited not merely on that side of the silver plate which faces the copper, but after about a minute on the other side also, showing that in this, as in other cases, the lines of force curve round.

A galvanometer included in the circuit, while the deposition was going on, indicated an electric current flowing through the liquid from copper to silver.

The original observations convinced the authors that the decomposition of the copper nitrate could not be due to the action of oxygen on the positive metal; but, to make the matter more certain, bright copper and silver plates in conjunction were immersed, the copper in a pure, *i.e.*, deoxygenised solution of copper nitrate, the silver in an oxygenised solution: the two liquids communicated through the diaphragm of a divided cell. In half an hour the silver plate was covered with a reddish film, while not a trace of tarnish was perceptible on the copper. On cleaning the plates, and reversing their position, the copper was oxidised, while the silver remained free from cupreous deposit. The authors believe, therefore, that, through the simultaneous action of the two metals, the dissolved salt is put into such a state of tension, that oxygen brings about a chemical change which would otherwise be impossible, and that this change is initiated in close proximity to the more negative metal.

The copper nitrate employed was prepared by the action of copper on pure silver nitrate, and varied in strength from 3.3 to 6.8 per cent.

Though only this particular reaction has been fully examined, the authors have satisfied themselves that it is not an isolated fact. Each of the elements concerned may be replaced by others: thus, the sulphate may be substituted for the nitrate of copper, or platinum may be used instead of silver; chlorine may take the place of oxygen, with production of the subchloride instead of the suboxide; and zinc may be employed as the positive metal, with zinc chloride as the salt in solution, in which case copper may be taken as the negative metal, and on its surface will form a deposit of oxide of zinc. A. T.

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### Iron Reduced by Hydrogen. By G. DRAGENDORFF (Pharm. J. Trans. [3], ii, 988—9).

COMMERCIAL "ferrum redactum" frequently contains oxide and sulphide, the latter resulting from basic sulphate in the ferric oxide, or from hydrogen sulphide in the hydrogen employed. To obtain a pure product, iron nails are dissolved in pure hydrochloric acid, the solution is precipitated by potassium oxalate, and the ferrous oxalate converted into ferric oxide by heating in air. The sulphuric acid in the hydrogen apparatus must be perfectly cold and dilute: the hydrogen should be passed over pumice soaked in lead nitrate, and then over fragments of caustic potash. The reduction should be effected in an iron tube 1.5 in. diameter at a bright white heat, as the iron is then more dense and less easily oxidised by air.

C. G. S.

**Composition of White Cast Iron.** By C. RAMMELSBERG  
(Deut. Chem. Ges. Ber., v, 430).

THE fracture of a rail-roller from the "Henrichshuette," near Hattingen, on the Ruhr, showed aggregations of regular octohedrons, which were analysed with the following results:—

Graphite.	Carbon.	Silica.	Sulphur.	Phosphorus.
1.121	1.963	1.537	0.113	0.041

The number of atoms of these elements and those of iron being in the ratio of 1 : 7.6, whilst in the crystallised iron from Gleiwitz, the ratio is 1 : 7.9; in that from Loelling, in Carinthia 1 : 12; in that from Rothehuette on the Hartz, 1 : 19; and in the iron from Lauchhammer, 1 : 21.

This seems to be a confirmation of the author's view previously expressed, viz., that cast iron does not form definite compounds with carbon, but is a mixture of the isomorphous elements, iron, carbon, silicon, and phosphorus.

Another white cast iron which was very slowly cooled under the slag during an interruption in the working of the Freisenbruch Works, was also crystallised, but not so distinctly as the other, and showed that peculiar netted appearance often seen in substances crystallising in the regular system. It contains—

Carbon.	Silica.	Phosphorus.	Sulphur.
2.820	0.334	0.086	0

but only a trace of graphite. According to Karsten, white cast iron contains no graphite at all; but this is not correct. Bromeis and the author found that "spiegeleisen" from Maegdesprung contains 16.5 per cent., and that from Lohhuette 28 per cent. of the total amount of carbon in form of graphite.

C. S.

**Crystalline Phosphide of Iron.** By J. SIDOT (Compt. rend., lxxiv, 1425).

IN this paper a new crystalline and magnetic combination of iron and phosphorus is described.

The author prepared a considerable quantity of phosphide in the ordinary manner by passing the vapour of phosphorus over metallic iron, and afterwards, with the intention of volatilising the excess of phosphorus, calcined the product in an ordinary crucible. On breaking the fused and cooled mass, the interior was found to be studded with beautiful crystals, many of which were nearly a centimeter in length. The crystals were right prisms with a square base; generally iridescent upon the surface; they were strongly magnetic, and possessed a hardness comparable to that of steel.

The results obtained in the analysis of this crystalline phosphide corresponded very accurately with the formula,  $\text{Fe}_3\text{P}$ . A small quantity of silicon was found, but this was obviously an accidental impurity.

No phosphide of this composition has been previously prepared. Hvoslef obtained a phosphide to which he attributed the formula,  $\text{Fe}_6\text{P}$ , but it was neither magnetic nor distinctly crystalline; and it is highly probable that the magnetic phosphide obtained by fusing together a mixture of vivianite, ferric oxide, and charcoal, contains metallic iron, which communicates to it its magnetic properties.

M. Daubrée, in commenting upon this phosphide, remarks, that a highly crystalline and magnetic iron phosphide has been already prepared by reducing at a high temperature native tricalcic phosphate in presence of iron, but the crystals so obtained are not sufficiently well defined to enable their system to be determined with certainty. In other respects it closely resembles the phosphide described by the author in the present paper.

Alluding also to the presence of phosphides in iron of meteoric origin, he thinks it highly probable that the crystals mentioned by Rose as occurring in certain specimens of meteoric iron, which he designated *rhabdite*, may prove to be identical with the phosphide under discussion. The crystals are certainly isomorphous, and an analysis of rhabdite only is wanting to establish beyond doubt the identity of the natural and artificial specimens.

J. W.

### Analysis of the Incrusted Surface of a Block of Jew's Tin.

By J. H. COLLINS (Chem. News, xxv, 271).

A BLOCK of Jew's-house tin from Tremethack Moor, recently purchased for the Royal Institution of Cornwall, was found to be partially covered by a hard and brittle brown incrustation, in some places as much as a quarter of an inch in thickness.

Specific gravity .....	5.64
Moisture evolved at 120° .....	6.25
Metallic Tin .....	0.43
Stannic chloride .....	1.66
Stannic oxide .....	90.62
Ferric oxide .....	1.04
Silica .....	0.41
	<hr/> 100.41

The crust therefore appears to be composed chiefly of stannic oxide, somewhat resembling the native variety of cassiterite called "wood-tin," but neither so hard nor so heavy. It has no doubt been formed by the slow oxidation of the outer surface of the block of metallic tin, the slowness of the change being perhaps indicated by the dense condition of the incrustation.

J. W.



**Action of Dilute Saline Solutions upon Lead.** By M. M. PATTISON MUIR (Chem. News, xxv, 656).

THE author's experiments show that a comparatively small quantity of pure nitrates (especially ammonium nitrate) dissolved in a large quantity of water causes that water to exercise a very powerful solvent action upon lead. Pure distilled water dissolves about 2 mgm. of lead per litre after 24 hours' exposure of the lead to the action of the water. Loch Katrine water (as supplied to Glasgow) dissolves about half as much lead as this. If a very small quantity of a soluble carbonate be present, the action of this solution on lead is scarcely perceptible. So also if to a water containing nitrates there is added a small quantity of a carbonate, the action which, were nitrates alone present, would be exercised on the lead, is rendered very much less energetic. Chlorides act like carbonates, but not to so great a degree, and sulphates also act similarly. The results of the experiments are embodied in the following table:—

Name of salt in solution.	Grams per litre.	Grains per gallon.	Lead dissolved.					
			Grams per litre.			Grains per gallon.		
			24 hrs.	48 hrs.	72 hrs.	24 hrs.	48 hrs.	72 hrs.
Ammonium nitrate ..	·02	1·4	13	—	25	·91	—	1·75
„ „ ..	·04	2·8	15	15	32	1·05	1·05	2·24
„ „ ..	·08	5·6	15	—	—	1·05	—	—
Potassium nitrate ..	·02	1·4	2	2	—	·14	·14	—
Sodium sulphate ..	·05	3·5						
Potassium nitrate ..	·04	2·8	·8	1	1·2	·05	·07	·08
Sodium sulphate ..	·212	14·7						
Potassium nitrate ..	·045	3·1	—	—	·3	—	—	·021
Potassium carbonate	·308	21·5						
Potassium nitrate ..	·078	5·4	—	—	·5	—	—	·035
Potassium carbonate	·504	35·2						
Calcium sulphate ....	·252	17·5	·4	—	·8	·02	—	·05
„ „ ....	·458	28·5	·4	—	1·	·02	—	·07
Potassium carbonate..	·31	21·7	—	—	·2	—	—	·014
„ „ ..	·516	36·1	—	—	·2	—	—	·014
Calcium chloride ....	·25	17·5	·5	·5	·5	·04	·04	·04
„ „ ....	·51	35·7	·3	—	·4	·28	—	·028
Sodium sulphate ....	·20	14·	—	—	·8	—	—	·05
„ „ ....	·40	28·	—	—	·5	—	—	·03
Ammonium nitrate ..	·02	1·4	—	—	1·8	—	—	·126
Calcium nitrate ....	·06	4·2						
Ammonium chloride	·02	1·4	—	—	·4	—	—	·028
Potassium carbonate	·10	7						
Sodium sulphate ..	·20	14	—	—	·1	—	—	·007
Sodium sulphate ..	·20	14						
Potassium carbonate	·04	2·8	—	—	·1	—	—	·007
Calcium chloride ..	·10	7						
Loch Katrine .....	—	—	1	1	1·5	·07	·07	·105
Distilled water .....	—	—	2	2	3	·15	·15	·21

**On a Double Sulphide of Gold and Silver.** By M. M. PATTISON  
MUIR (Chem. News, xxv, 654).

THIS new sulphide was formed by the action of molten sulphur upon a mixture of gold and silver in a fused state. It is a dark grey crystalline substance, brittle, decomposed by heating in a current of hydrogen; fused with sodium carbonate it gives sodium sulphide, and a seeming alloy of gold and silver.

The following are the results of the analyses, and the percentage composition calculated for the formula,  $2(\text{Au}_2\text{S}_3) \cdot 5(\text{Ag}_2\text{S})$ .

S .....	15.85	16.17
Ag .....	48.68	49.27
Au .....	35.47	35.69
	<hr/>	<hr/>
	100.00	101.13

The specific gravity for this sulphide is 8.159.

M. M. P. M.

**A New Platinum Chloride.** By SIDNEY A. NORTON (J. pr.  
Chém. [2], v, 365).

THE author has obtained a well-crystallised, hydrated platinum chloride of the composition,  $\text{PtCl}_4 \cdot 5\text{aq.}$ , which does not deliquesce on exposure to the air, and yields a precipitate with ammonium chloride after some time only, or on warming. Four only of the five molecules of water are driven off at  $100^\circ$ . To prepare it, solutions of platinic chloride (1 mol.) and silver nitrate (2 mols.) are mixed; a double compound of silver and platinum chlorides is then precipitated, and a yellowish-red solution is formed, from which the above salt crystallises on evaporation over sulphuric acid.

H. E. A.

## Mineralogical Chemistry.

**Analysis of Genthite (Nickel-Gymnite) from North Carolina.**  
By F. P. DUNNINGTON (Chem. News, xxv, 270).

ALTHOUGH the occurrence of genthite in the neighbourhood of Webster, Jackson Co., N. C., has been reported, no specimens obtained directly from that locality have, up to the present time, been submitted to analysis.

The mineral occurs as an incrustation, usually not more than a millimeter in thickness, of delicate apple-green colour, and resinous lustre, translucent, and capable of being completely decomposed by hydrochloric acid. Sp. gr. 2.48.

The following numbers were obtained:—

$\text{SiO}_2$ .	$\text{MgO}$ .	$\text{NiO}$ .	$\text{FeO}$ .	$\text{H}_2\text{O}$ .
49.89	22.35	16.60	0.06	12.36 = 101.26

The analysis is not very satisfactory, but from insufficiency of material it could not be repeated. But assuming the above numbers to be correct, they do not correspond to the formula usually assigned to genthite, viz.  $[\frac{2}{3}(\text{MgO} \cdot \text{NiO}) + \frac{1}{3}\text{H}_2\text{O}]_2\text{SiO}_2 + \frac{4}{3}\text{H}_2\text{O}$ , but more nearly represent a nickel-aphrodite  $(\text{MgO} \cdot \text{NiO})\text{SiO}_2 + \frac{3}{4}\text{H}_2\text{O}$ .

Another mineral obtained from the same locality was also examined. In appearance it much resembled Silesian pimelite, but proved to contain no nickel. It was massive, with indistinct traces of fibrous structure, moderately brittle, with earthy fracture, and of a slightly yellowish apple-green colour. Hardness, about 1.25; sp. gr., 2.3. It was infusible before the blowpipe, gave off water when heated in a closed tube, and was partly, but not completely, decomposed by hydrochloric acid.

It gave on analysis—

$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{NaO}$ .	$\text{H}_2\text{O}$ .
43.87	22.21	16.14	1.05	16.37 = 99.64.

These figures lead to a complex and somewhat doubtful formula, which does not correspond with that of any hitherto-described species.

J. W.

#### Analysis of Compact Talc from North Carolina. By J. B. ADGER (Chem. News, xxv, 270).

THIS mineral was a very beautiful specimen of "soapstone," distantly resembling the finer and lighter-coloured varieties of Chinese jade or nephrite. It was of a greenish-white colour, uniform and compact in character, with an indistinctly foliated structure. Hardness, 1.25. Sp. gr., 2.82.

Analyses afforded—

$\text{SiO}_2$ .	$\text{MgO}$ .	$\text{Al}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{H}_2\text{O}$ .
57.72	33.76	2.52	0.64	6.01 = 100.65.

If the silica, magnesia, and water alone be considered, the above numbers correspond very fairly with the formula  $(\frac{2}{3}\text{MgO} \cdot \frac{1}{6}\text{H}_2\text{O})\text{SiO}_2 + \frac{1}{6}\text{H}_2\text{O}$ .

J. W.

## Organic Chemistry.

#### Synthesis of Condensed Hydrocarbons. By D. AMATO (Gazzetta Chimica Italiana, ii, 6—9).

THE spongy mass remaining in the retort in the distillation of castor-oil, melts and distils at a higher temperature, yielding a product consisting principally of a mixture of hydrocarbons. By careful fractional distillation a portion was obtained, boiling below  $200^\circ$ , which, after treatment with fuming sulphuric acid to remove the olefines,  $\text{C}_n\text{H}_{2n}$ , was washed, dried, and re-distilled. By this means a hydrocarbon



$C_7H_{16}$ , hydride of heptyl, was separated, boiling between  $95^\circ$  and  $100^\circ$ , and another the hydride of undecyl,  $C_{11}H_{24}$ , boiling between  $180^\circ$  and  $185^\circ$ . The portions boiling at  $140^\circ$  to  $145^\circ$ ,  $160^\circ$  to  $165^\circ$ , and  $195^\circ$  to  $200^\circ$ , were also analysed, and found to consist of saturated hydrocarbons. They are all liquid at the ordinary temperature, insoluble in water, slightly soluble in alcohol, and miscible in all proportions with ether.

C. E. G.

**Nitro-compounds of the Fatty Series. Nitroethane.** By V. MEYER and O. STÜBER (*Deut. Chem. Ges. Ber.*, v, 399—406).

INSTEAD of yielding amine bases with nascent hydrogen, the nitrous ethers split up into alcohol and ammonia. From this it follows that the constitution of ethyl nitrite is expressed by the formula,  $C_2H_5-O-NO$ , and not by  $C_2H_5.NO_2$ , the formula of the real nitro-compound. The authors have already pointed out (*Deut. Chem. Ges. Ber.*, v, 203) that the reaction of silver nitrite with the iodides of the alcohol-radicals supplies us with a method of forming the nitro-compounds of the fatty series.

Ethyl iodide at once acts upon silver nitrite, and the resulting nitroethane can easily be obtained quite pure by distillation and rectification in an oil-bath. Nitroethane is a highly refractive liquid, entirely devoid of colour, and possessing an agreeable and peculiar ethereal odour. It does not mix with water. Its specific gravity is 1.0582, and its boiling point is  $111^\circ$ — $113^\circ$  (nitrous ether boils at  $16^\circ$ ). Its vapour has a density of 36.9 ( $H = 1$ ), the calculated number for  $C_2H_5.NO_2$  being 37.5. The vapour is inflammable, and burns with a pale-yellow flame, but does not detonate when heated, even much above the boiling point. The nitro-compound in the amyl series has also been obtained, but not quite pure.

In the preparation of nitroethane some nitrous ether is always formed, and about one-fifth of the ethyl iodide always escapes decomposition, even when it is heated for a long time in a sealed tube with excess of silver nitrite.

Nitroethane is converted into amidoethane (ethylamine) by the action of iron and acetic acid. The reaction requires to be started by the application of heat, but then becomes violent, and if it be desired to obtain the ethylamine pure, the action must be so moderated by immersing the flask in cold water that the liquid never boils. On distilling the product with caustic potash, and receiving the vapours in dilute hydrochloric acid, ethylamine hydrochloride is at once obtained quite pure. This salt can be obtained in this way in prismatic crystals of great beauty, which are very deliquescent.

Nitroethane dissolves in a solution of potash with evolution of heat, and the solution can be boiled without the nitroethane being given off, but it is set free on supersaturating the solution with dilute sulphuric acid. It also dissolves in ammonia-water, but is then gradually decomposed. It appears, therefore, to possess weak acid properties. It does not dissolve in baryta-water. On heating it with sodium, gas is evolved, and a dazzling white powder is obtained; this, when gently

heated, explodes violently, and is, perhaps, analogous to fulminating silver, fulminic acid being nitro-acetonitrile [in this respect it is like the sodium and other metallic salts of trinitrophenol].

Kept for some hours in a sealed tube at  $100^{\circ}$ , with a concentrated solution of caustic potash, it is decomposed, much ammonia being liberated, and potassium nitrite and an oily body smelling like peppermint being also produced; whether alcohol is produced could not be ascertained, because of this oily body.

E. D.

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**Two New Isomerides of Propylene Bromide.** By E. REBOUL  
(Compt. rend., lxxiv, 613—616).

THE author has previously shown that monobromomethylene and monobromopropylene unite with hydrobromic acid, yielding either the dibromides of propylene and ethylene, or the bromhydrides of monobromopropylene and monobromomethylene, according to the concentration of the acid employed. The aqueous solution saturated with the acid at  $+6^{\circ}$ , yields the dibromides only, whilst the same solution diluted with a third of its volume of water, gives only the bromhydrides. Intermediate strengths of air yield mixtures of the above compounds.

By the action of hydrobromic acid saturated at  $+6^{\circ}$  on allyl bromide, a mixture of two isomeric bodies is produced; the first of these boils at  $143^{\circ}$ — $145^{\circ}$ , and is found to be identical in composition and properties with propylene dibromide, while the second, which boils at  $162^{\circ}$ , is found by its decomposition with alcoholic potash to be the hydrobromide of allyl bromide. Allylene unites directly in the cold with hydrobromic acid, giving rise to two compounds, the principal of which is the dihydrobromide of allylene, boiling at  $114^{\circ}$ , and isomeric with the hydrobromide of allyl bromide; the second is the monohydrobromide of allylene,  $C_3H_4.HBr$ , a liquid boiling at  $48^{\circ}$ , isomeric with brominated propylene. The author will return to this subject in a future paper.

A. P.

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**Identity of the Hydrobromide and Hydriodide of Bromopropylene with the Dihydrobromide and Hydrobromiodide of Allylene. Dihydrobromide of Acetylene.** By E. REBOUL  
(Compt. rend., lxxiv, 944—948).

In a previous paper the author has mentioned that bromopropylene combines with a concentrated aqueous solution of hydriodic acid, yielding a hydriodide boiling at  $147^{\circ}$ — $148^{\circ}$ . This body, by the action of alcoholic potash, gives rise to the hydrobromide of allylene boiling at  $48^{\circ}$ — $49^{\circ}$ . This last-named body, by the action of hydriodic acid, yields an hydrobromiodide of allylene boiling at  $147^{\circ}$ — $148^{\circ}$ , and identical with the hydriodide of bromopropylene. The only difference which exists between the two reactions is, that the action of hydriodic acid on hydrobromide of allylene takes place with far greater ease than in the other case. It is probable that the hydriodic acid first transforms the bromopropylene into hydrobromide of allylene,

with which it then combines. In the same way the author has proved the identity of the hydrobromide of bromopropylene with dihydrobromide of allylene, as by the action of potash the two bodies yield the same substance, the monohydrobromide of allylene.

By the decomposition of the hydrobromide of bromethylene with alcoholic potash, a body was obtained which was identical with bromethylene, boiling at  $17^{\circ}$ — $18^{\circ}$ ; both these latter bodies, by the action of hydrobromic acid, behave in a similar manner.

The long-continued action of hydrobromic acid on acetylene yields the dihydrobromide of acetylene, which is found to possess the same composition and boiling point as the hydrobromide of bromethylene.

A. P.

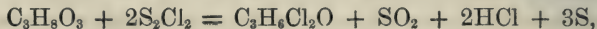
**The Non-existence of Gerhardt's Parathionic Acid.** By C. SCHEIBLER (Deut. Chem. Ges. Ber., v, 446).

ERLENMEYER has lately shown that this acid does not exist; and now the author calls attention to the fact that he proved the non-existence of this acid already in 1862, in a paper read before the Naturforscher Versammlung, at Karlsbad. On boiling a solution of barium ethylsulphate and neutralising the free acid from time to time, it can be completely converted into barium sulphate, whereas, if the operation is interrupted as soon as 90 per cent. is decomposed, the solution contains only pure barium ethylsulphate.

C. S.

**Dichlorhydrin.** By AD. CLAUS (Deut. Chem. Ges. Ber., v, 353—358).

FOR the preparation of dichlorhydrin the method originated by Carius, which consists in treating anhydrous glycerin with sulphur chloride, seems to be the best. The reaction proceeds according to the equation—



though sulphuretted by-products are simultaneously formed, and from 200 grams of glycerin only 150 to 160 grams of pure dichlorhydrin are obtained.

Dichlorhydrin oxidised by chromic acid gave a body which, though not yet fully examined, is believed to be a dichloracetone.

The action carried further gave rise to chloracetic acid, which was formed in considerable quantity, and then hydrochloric acid and carbon dioxide, probably together with formic acid.

*Diiodhydrin*, the existence of which has hitherto been doubted, was obtained by heating dichlorhydrin with iodide of potassium and a little water. Diiodhydrin is a slightly yellow, viscid oil of specific gravity 2.4, freezing at  $16^{\circ}$ — $20^{\circ}$  below zero into a white crystalline mass. It is decomposed by distillation, giving amongst other products, allyl alcohol and iodide.

By the action of weak solutions of ammonia on dichlorhydrin, a base is generated which is probably identical with the glyceramine of



Berthelot and Luca. The formula, however, is not  $C_3H_9NO_2$ , as hitherto represented, but  $C_3H_7NO$ . In acting upon the dichlorhydrin, the ammonia has thus first removed  $HCl$  and then substituted  $NH_2$  for  $Cl$ .

The analytical numbers obtained by Berthelot and Luca in the analysis of the platinum salt partly support this view, and new platinum determinations gave 35.5 and 35.2 per cent. of platinum instead of 35.4, the proportion required by the formula  $C_3H_7NO$ . The author names the base *glycidamine*.

When dichlorhydrin is heated with concentrated alcoholic ammonia, an entirely different decomposition occurs. Sal-ammoniac, and a gelatinous substance are formed; the latter is insoluble in water, alcohol, ether, and acids, and appears to be identical with the compound obtained by Reboul from the monochlorhydrin of glycide. Analysis leads to the formula  $C_{12}H_{27}Cl_2N_3O_4$ . By destructive distillation, or better, by heating with lime, this body, which the author calls *chlorhydrinimide*, yields a basic oil, the smell of which recalls that of nicotine. Dr. Nahmacher, who has taken part in this research, is continuing the investigation of this substance.

W. A. T.

**Dichloroglycide.** By AD. CLAUS (Deut. Chem. Ges. Ber., v, 358—362).

THE author, in conjunction with Dr. Kölver, has made some experiments with the view of converting Reboul's dichloroglycide into the corresponding allyl glycol. Experiments with silver acetate gave a negative result. On heating it with potassium acetate in alcoholic solution, potassium chloride was certainly formed, and the addition of water threw down a part of the acetic ether, whilst part remained in solution. Neither fraction could, however, be obtained of constant boiling point or free from chlorine.

Dichloroglycide heated with cyanide of potassium dissolved in alcohol, gave potassic chloride, and a dark-coloured solution from which ammonia was evolved, and which had the smell characteristic of volatile cyano-compounds. When it was submitted to distillation, nothing could be obtained from the distillate; but by treating the black residue with potash, ammonia was abundantly evolved and two acids were formed, one of which gave a lead salt soluble in water, the other insoluble.

The former is uncrystallisable, and appears to possess the composition of an oxycrotonic acid.

The second acid is tricarballic acid, melting at  $158^\circ$ — $159^\circ$ .

This formation of tricarballic acid is not due to the accidental presence of trichlorhydrin in the dichloroglycide from which it was obtained, nor is dichloroglycide a mixture of a monochloride with trichlorhydrin. Experiments undertaken for the purpose of clearing up doubts on this point, show that it is a homogeneous body.

W. A. T.

**Researches on the Derivatives of Glycerin. V.** By L. HENRY  
(Deut. Chem. Ges. Ber., v, 449—458).

ALLYL alcohol combines with hypochlorous acid, forming monochlorhydrin; the yield is, however, only small, as a great portion of the alcohol undergoes oxidation. Better results are obtained by using the ethers of allyl alcohol.

*Monooethyl-chlorhydrin*,  $C_3H_5Cl(OH)OC_2H_5$ , is produced by shaking allyl-ethyl ether with cold dilute hypochlorous acid; the reaction is rather violent, and the liquid must therefore be kept cold. It is a thick colourless liquid boiling at  $183^{\circ}$ — $185^{\circ}$ , and possessing a faint ethereal and refreshing odour. It dissolves in fuming nitric acid with formation of the nitrate,  $C_3H_5Cl(OC_2H_5)NO_3$ ; and on distilling it with caustic potash, it is converted into *ethylglycide*,  $C_3H_5 \left\{ \begin{smallmatrix} OC_2H_5 \\ O \end{smallmatrix} \right.$ , a colourless, mobile liquid, possessing an agreeable odour and very pungent taste. It is soluble in water, and combines readily with the haloïd hydracids; phosphorus pentachloride converts it into  $C_3H_5(OC_2H_5)Cl_2$ , a body which is also produced by the addition of chlorine to allyl-ethyl ether. These bodies have already been obtained by Reboul, but only in an impure state.

In dichlor- and dibromoglycide, the two atoms of haloïd elements have different values; one of them is easily exchanged by double decomposition, whilst the other is eliminated by the action of alkalis as a hydracid.

Just as allyl bromide with silver nitrate yields *allyl nitrate*, a mobile liquid boiling at  $106^{\circ}$ , and having a pungent smell, so dibromoglycide is converted by the same reagent into *monobromallyl nitrate*,  $C_3H_4BrNO_3$ , a mobile liquid,\* possessing an agreeable odour and a sweetish, pungent taste.

*Monobromallyl acetate*,  $C_3H_4Br.C_2H_3O_2$ , is produced by the action of dibromoglycide upon potassium acetate. It is a mobile liquid boiling at  $163^{\circ}$ — $164^{\circ}$ , and having a pleasant, refreshing odour; it is not acted upon by the chlorides of phosphorus. By distilling it with caustic soda, it yields *monobromallyl alcohol*,  $CH_2.CBr.CH_2.OH$ , a mobile liquid boiling at  $155^{\circ}$ , and having also an agreeable odour. By the action of phosphorus pentachloride the alcohol is converted into *monobromallyl chloride* ( $C_3H_4Br$ )Cl, a heavy liquid boiling at  $120^{\circ}$ , and most probably identical with Reboul's chlorhydrobromoglycide.

By heating the alcohol with an alcoholic potash-solution, a distillate is obtained showing the reactions of the propargyl-compounds, and containing most probably *propargyl-alcohol*, which, however, could not be isolated.

By the action of potassium acetate upon dichloroglycide, a mixture of several products is obtained, among them being a small quantity of monochlorallyl acetate, whilst when dichloroglycide is heated with potassium sulphocyanate, pure monochlorallyl sulphocyanate is produced.

*Methyl-allyl ether*,  $CH_3OC_3H_5$ , obtained by the action of sodium

\* The author says that from the alcoholic solution it is precipitated by water as a *thick* oily liquid, but afterwards describes it as a *mobile* fluid.



methylete on allyl bromide, is a liquid boiling at  $46^{\circ}$ . Its dibromide,  $\text{CH}_3\text{OC}_3\text{H}_5\text{Br}_2$ , boils at  $185^{\circ}$ , and yields by distillation over solid caustic soda, *methyl-monobromallyl ether* boiling at  $115^{\circ}$ — $116^{\circ}$ , together with some *methyl-propargyl ether*,  $\text{CH}_3\text{OC}_3\text{H}_3$ . The latter body is obtained pure when methyl-monobromallyl ether is heated with an alcoholic potash-solution; it boils at  $61^{\circ}$ — $62^{\circ}$ .

*Amyl-propargyl ether*,  $\text{C}_5\text{H}_{11}\text{OC}_3\text{H}_3$ , is a limpid liquid boiling at  $140^{\circ}$ — $145^{\circ}$ , and having hardly any odour.

*Phenyl-allyl ether*,  $\text{C}_6\text{H}_5\text{OC}_3\text{H}_5$ , is produced by the action of sodium phenylate upon allyl bromide. It is a colourless, strongly refracting liquid, boiling at  $192^{\circ}$ — $195^{\circ}$ , and having the same density as water. It combines with bromine, but at the same also substitution in  $\text{C}_6\text{H}_5$  takes place.

When diallyl tetrabromide is heated with solid caustic potash, a product is formed containing *dibromodiallyl*,  $\text{C}_6\text{H}_8\text{Br}_2$ . On heating this with an alcoholic potash solution, it is converted into *diallylene*,  $\text{C}_6\text{H}_6$ , an isomeride of benzene. It is a very refractive liquid, boiling at about  $85^{\circ}$ . It burns with a luminous and smoky flame, and combines under explosion with bromine. With an aqueous solution of silver nitrate, it gives a white, amorphous precipitate insoluble in ammonia and exploding when heated below  $100^{\circ}$ .

C. S.

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**Phenomena exhibited by Iodide of Starch.** By E. DUCLAUX  
(Ann. Chim. Phys. [4], xxv, 264—284).

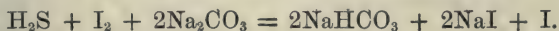
IODIDE of starch has been considered by some chemists to be a definite chemical compound. The author, however, considers that it is merely a case of molecular adhesion, and that the iodide is a true solution of iodine in starch, using that term in a very general sense. He bases his view on several of the physical and chemical characteristics of this body. In the first place, the composition of the iodide is by no means constant, as it can be obtained with the iodine varying from 2 to 41 per cent. Payen and Fritsche considered that it was a compound of 10 atoms of starch with one of iodine, containing 7.2 per cent. of the latter. Different methods of preparation, however, give products which vary very greatly in their composition. The formation of iodide of starch in solution depends essentially on three conditions—1, on the quantity of starch present; 2, on the amount of iodine present; and 3, on the quantity of water used. To prove the last case, the author takes a standard weight of starch, dissolved in different quantities of water, and adds a sufficient quantity of iodine to produce the blue coloration. Thus 100 milligrams of starch dissolved in 50 c.c. of water require 1.1 c.c. of a solution of iodine in water to produce the blue coloration. If, however, 800 c.c. of water are used instead of 50, it requires 4.0 c.c. of iodine solution, and if diluted to 3,200 c.c., it takes 23.4 c.c. of solution. These numbers show that in the presence of large quantities of water a considerable excess of iodine must be added to produce the blue colour. It thus seems necessary for the solution to contain a certain ratio of iodine before its action on starch will commence. It was also noticed that the blue colour obtained in presence of excess



of starch gradually disappears, and that the addition of a drop of chlorine water to the decolorised solution will bring back its colour with the original intensity, showing that the iodine in the presence of excess of starch is probably converted into hydriodic acid. When iodine is added to a standard volume of solution containing varying quantities of starch, it is found that as the quantity of starch grows smaller, so does the quantity of iodine required to produce the blue colour. Likewise, if to a blue solution of starch distilled water is added, the blue colour is considerably decreased, even when due allowance is made for the dilution of the liquid. The author has made some experiments on the blueing of starch in alkaline solutions by iodine, such as sodic hydrate, sodic carbonate, and hydro-sodic carbonate. The sodic carbonate is supposed to be without action on solution of iodine, yet a considerable amount of iodine must be added to a dilute solution of sodic carbonate containing starch before the blue colour appears. The quantity of iodine required varies proportionally with the amount of sodic carbonate in solution, the iodine used being sufficient to attack  $\frac{8}{1000}$  of the sodic carbonate. The addition of a few drops of hydrochloric acid to an alkaline solution containing a small quantity of iodine with starch gives rise to an intense blue colour. This is difficult to explain, on the supposition that a small quantity of an iodide was present, as the hydriodic acid liberated is without action on starch. The hydric sodic carbonate is without action on solution of iodine in water, the first drop of the latter being sufficient to produce the blue coloration in presence of starch. Sodic sulphide solution acts on iodine, and it is curious that the combined effect of a mixture of sodic sulphide and carbonate is considerably greater than that of the same solutions when separate. Payen and Gobley have found that if alcohol is added to a solution containing a small quantity of iodide of starch, it is completely decolorised; and Goppelsröder and Schönbein have found that certain salts, such as the sulphates of potassium, ammonium, sodium, magnesium, and aluminium, have the property of masking to some extent the reaction of iodine upon starch.

The action of heat upon iodide of starch is also dependent on the amount of the body in solution. Thus, starch-solution, to which 30 drops of iodine-water were added, was decolorised at 55°; a similar solution, with 60 drops of iodine-solution, became colourless at 75°; and a third, to which 280 drops were added, was decolorised at 90°. The substance which is called iodide of starch does not, therefore, possess any of the properties of a definite compound. It is not produced immediately on the meeting of the elements which give rise to it; the moment at which the action commences depends on the state of dilution of the liquid, on its temperature, and on the nature and proportion of the substances which it contains. It is a simple case of molecular adhesion, liable to the same disturbances as other cases of this class. There are some other substances which are coloured blue by iodine, as, for instance, the gelatinous subacetate of lanthanum. Some of these observations have considerable importance on volumetric estimations by iodine when starch is used as an indicator. To ensure the greatest possible exactness, the solution at the end of the analysis should be made as nearly neutral as possible. In the case of estimations of

hydric sulphide, a rough determination of the amount is made, and two molecules of sodic carbonate are added for every one of hydric sulphide; another determination is then made, giving the following equation:—



At the end of the reaction sodic bicarbonate will be obtained, which will be without action on the iodine. In the estimation of arsenious acid, it is better for the same reason to work with hydrosodic carbonate, and not with sodic carbonate.

A. P.

**Derivatives of Acrylic Acid.** By E. LINNEMANN (Ann. Chem. Pharm., clxiii, 95).

ACRYLIC acid boils at a temperature nearly the same as the boiling point of propionic acid, but is converted into a crystalline mass at  $+7^\circ$ . and moreover has a tendency to pass into a white amorphous mass, analogous to disacryl in properties. It combines with hydriodic, hydrobromic, and hydrochloric acids, forming substituted propionic acids. The compound with hydriodic acid is identical with *glycerin-iodopropionic acid*; that with hydrobromic acid is identical with the *isobromopropionic acid* of Richter, obtained by bromine and iodopropionic acid; but the hydrochloric acid compound melts  $20^\circ$  lower than  $\beta$ -chloropropionic acid, Wichelhaus giving the melting point of glycerin chloropropionic acid at  $65^\circ$ ; and Richter of the acid from iodopropionic acid and chlorine, at  $58^\circ$ ; while the acrylic acid derivative melts at  $40.5^\circ$  (corrected). The ethylic ether of this acid also boils at a higher temperature than the chloropropionic ether of Wichelhaus.

Further experiments are in progress.

C. R. A. W.

**The Monochlorocrotonic Acid obtained from Crotonic Chloral.** By C. SARNOW (Deut. Chem. Ges. Ber., v, 467—472).

THE author, who has already given a short account of this acid (Deut. Chem. Ges. Ber., iv, 731, and this Journal, xxiv, 1046), finds that it is not identical with the monochlorotetraacrylic acid obtained by Geuther (*Jena. Zeitschr.*, vi, and this Journal, xxiv, 813) from ethyl-diacetic acid by the action of phosphoric pentachloride, since it does not yield tetrolic acid,  $\text{C}_4\text{H}_4\text{O}_2$ , by treatment with potassium hydrate, and, moreover, differs in the crystallisation of the silver-salt, which forms fine long needles. It melts at  $96^\circ$ , and distils at  $212^\circ$ . The chlorine is not removed from the acid, in aqueous solution, either by zinc dust or silver oxide, or by heating it with ammonia to  $120^\circ$ . When, however, a concentrated solution of sodium monochlorocrotonate is treated with sodium-amalgam, crotonic acid is produced. This melts at  $72^\circ$ , and is identical in all other respects with that obtained from allyl cyanide, and by Kekulé from crotonic aldehyde. From the difficulty with which the chlorine is removed, the author believes that in



this acid, it is directly combined with the carbon atom, which, moreover, is not united to hydrogen. *Potassium monochlorocrotonate*,  $C_4H_4ClO_2K$ , is very readily soluble in water, and crystallises therefrom in needles, and from its alcoholic solution in plates. The *sodium salt*,  $C_4H_4ClO_2Na$ , is uncrystallisable. The *ammonium salt*,  $C_4H_4ClO_2NH_4$ , forms large plates, or six-sided tables, which sublime readily at  $100^\circ$ . The *silver salt*,  $C_4H_4ClO_2Ag$ , is somewhat difficultly soluble in water, from which it crystallises in long white needles. The *lead salt*,  $(C_4H_4ClO_2)_2Pb + H_2O$ , forms glistening plates and needles. The *basic cupric salt*,  $(C_4H_4ClO_2)_2Cu.Cu(OH)_2$ , is precipitated as an amorphous bright blue powder, on adding cupric sulphate to a solution of an alkaline monochlorocrotonate; the *neutral salt*, which forms fine prisms of a blue colour, is obtained by evaporating over sulphuric acid a solution of cupric carbonate in the acid; the *calcium salt*,  $(C_4H_4ClO_2)_2Ca$ , crystallises in thick prisms, and the *barium salt*  $(C_4H_4ClO_2)_2Ba$ , in thin plates which are more readily soluble than the calcium salt. *Ethyl monochlorocrotonate*,  $C_4H_4ClO_2.C_2H_5$ , formed on saturating an alcoholic solution of the acid with hydrochloric acid, is a colourless liquid, having a pleasant fruity odour, and boiling at  $176^\circ$ .

*Monochlorocrotonitrile*,  $C_4H_4ClN$ , prepared in the usual way by the action of phosphoric anhydride on the amide, is a colourless, highly refractive liquid, boiling at  $136^\circ$ .

*Monochlorodibromobutyric acid*,  $C_4H_5ClBr_2O_2$ . On adding a molecule of bromine to a solution containing a molecule of monochlorocrotonic acid, the two unite, forming monochlorodibromobutyric acid, which separates as a colourless oil, soon becoming crystalline. It is somewhat difficultly soluble in cold water, readily soluble in alcohol, and still more so in ether. It forms lustrous prisms, which melt at  $92^\circ$ . The salts of monochlorodibromobutyric acid are very readily soluble in water, with the exception of the compounds of silver lead and mercury. The *silver salt*,  $C_4H_4ClBr_2O_2Ag$ , is a white crystalline precipitate, difficultly soluble in water, readily in ammonia. The *lead salt*,  $(C_4H_4ClBr_2O_2)_2Pb + H_2O$ , is precipitated in needles, and the *mercury salt* from a moderately concentrated solution, as white needles. Monochlorodibromobutyric acid and its salts are decomposed when boiled with water, hydrobromic acid or a bromide being formed, carbonic anhydride evolved, and a neutral oil distilling over with the aqueous vapour. This oil decomposes in the presence of water, but can be distilled unchanged when dry. As the analytical results were unsatisfactory, the author believes that *monochloromonobromopropylene* is first formed, which, in the presence of water, undergoes further decomposition.

On subjecting monochlorodibromobutyric acid to dry distillation, or by treating it with zinc and hydrochloric acid, monochlorocrotonic acid is regenerated.

Crotonic chloral, when treated with zinc-dust and water, or with zinc and hydrochloric acid, appears to yield monochlorocrotonic aldehyde, but the author has, as yet, been unable to separate it from the crotonic aldehyde formed at the same time.

C. E. G.



**Some Properties of Chloral Hydrate.** By T. L. PHIPSON  
(Chem. News, xxv, 257).

WHEN chloral combines with water to form the solid hydrate, it gives out a considerable amount of heat, but when chloral hydrate dissolves in water, a large proportion of this heat is re-absorbed. Half a pound of chloral hydrate mixed rapidly with half a pound of water, causes the thermometer to sink many degrees below zero. The crystalline form of pure chloral hydrate is the oblique rhombic prism, and the crystals are usually very well defined; when the prisms are short, as is sometimes the case, they are liable to be mistaken for acute rhombohedrons.

When minute fragments of the crystals remain suspended on the surface of pure distilled water, they move about rapidly, with the same peculiar gyratory motion that is noticed with camphor under the same circumstances.

J. W.

**Carbothialdine.** By A. D. CLAUS (Deut. Chem. Ges. Ber., v, 362—364).

CARBOTHIALDINE is formed by the action of carbon disulphide on aldehyde ammonia. It cannot be crystallised from water or from alcohol, without decomposition and loss, but from concentrated aqueous ammonia it is deposited in magnificent large crystals.

Starting from the idea that carbothialdine was a kind of sulphur urea, it was hoped that interesting decomposition-products would be obtained by the action of iodine, nitrous acid, or mercuric chloride, but in each case the results were aldehyde, carbon disulphide, ammonia, and ammonium sulphocyanide. It is noteworthy in the case of mercuric chloride, that when one molecule was boiled with one molecule of carbothialdine in aqueous or alcoholic solution, the whole of the mercury was quickly precipitated as sulphide, whilst aldehyde, sal-ammoniac, hydrochloric acid, and hydrosulphocyanic acid were produced.

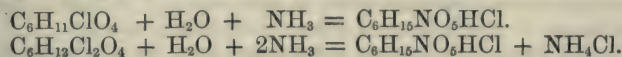
But when a large excess of mercuric chloride was employed, a white precipitate was deposited which became crystalline on boiling without the production of a trace of aldehyde.

Determinations of carbon, hydrogen, and sulphur confirmed the formula originally given by Liebig and Redtenbacher.

W. A. T.

**New Organic Base from Sugars.** By G. BOUCHARDAT (Compt. rend., lxxiv, 1406—1408).

ONE part of monochlorhydric dulcitate,  $C_6H_{11}ClO_4$ , or of dichlor- or dibromhydric dulcite,  $C_6H_{12}Cl_2O_4$ , heated for six hours to  $100^\circ$  with 10 pts. of alcoholic ammonia, yields ammonia and dulcitamine hydrochloride. The latter may be dissolved out by absolute alcohol and precipitated in long needles by very gradual addition of ether:



The salt is very soluble in alcohol or water, very slightly in ether-alcohol. The aqueous solution is neutral and has a faintly sweet taste. Treated with silver oxide, it yields free dulcitamine as a powerful base analogous to glyceramine, strongly blueing litmus, expelling ammonia from its combinations, absorbing carbon dioxide from the air, and forming by evaporation an uncrystallisable syrup, which gives with acids neutral salts crystallising with difficulty. The hydrochloride forms with platinic chloride orange-yellow needles of the salt,  $2\text{C}_6\text{H}_{15}\text{NO}_5\text{HCl.PtCl}_4$ , very soluble in water and absolute alcohol, but not in ether, decomposed on heating, with a smell of burnt sugar and burnt horn. Auric chloride gives a difficultly crystallisable compound.

C. G. S.

### Researches on the Constitution of the Benzene-Derivatives.

By V. v. RICHTER (Deut. Chem. Ges. Ber., v, 422—429).

THE author has shown in a former communication that by heating the three bromonitrobenzenes with potassium cyanide, the ortho- and the meta-compound are converted into the nitriles of the corresponding bromobenzoic acids, whilst parabromonitrobenzene is not acted upon at all. He has now studied the action of potassium cyanide upon the two isomeric bromonitrotoluenes which are produced, as Wroblevsky and Kurbatow have found, by the action of nitric acid upon pure parabromotoluene.

The solid compound is parabromo-metanitro-toluene, because Huebner obtained from it metatoluidine. On heating it with an alcoholic solution of potassium cyanide to  $200^\circ$ , and boiling the product with an alcoholic solution of potash, a bromotoluic acid is produced, which by the action of nascent hydrogen yields a toluic acid melting at  $108^\circ$ — $109^\circ$ , and yielding on oxidation with chromic acid, isophthalic acid. The acid obtained was therefore isotoluic acid, which, according to Ahrens, melts at  $90^\circ$ — $93^\circ$ ; according to Tawildarow, at  $85^\circ$ ; and according to Wurtz, at  $90^\circ$ . But the acids obtained by these chemists were probably not pure, and it is well known that the melting point of an aromatic acid is lowered when traces of impurities are present.

Wurtz obtained his isotoluic acid, together with paratoluic acid, by oxidising crude bromotoluene, which is a mixture of para- and meta-bromotoluene not containing any orthobromotoluene.

From these observations, it appears that the meta-derivatives of toluene belong to the same series as isophthalic acid, in which the two carboxyls occupy the positions 1—3. But according to v. Meyer, the side-chains in these meta-compounds have the positions 1, 2, and this view finds a confirmation in the fact that W. Remsay and R. Fittig obtained orthotoluic acid from toluene-metasulphonic acid.

We must therefore assume that either in the latter reactions or in those of the author, a molecular change has taken place. This question would, however, assume quite a new aspect if Kekulé's mechanical hypothesis of the linking of atoms were found correct.

The liquid bromonitrotoluene is not acted upon by potassium cyanide

at all, the probable reason being that the nitro-group occupies the ortho-position, and is too far distant from the bromine, just as in the case of parabromonitrobenzene; moreover, it is protected by the neighbourhood of the methyl.

C. S.

**Ready Liberation of Hydrocyanic Acid from Nitrobenzene, Dinitrobenzene, and Similar Compounds.** By J. POST and H. HÜBNER (Deut. Chem. Ges. Ber., v, 408).

WÖHLER pointed out in 1828 the remarkable fact that picric acid yields hydrocyanic acid by treatment with baryta-water. The authors have obtained the same result with solution of caustic potash. They also find that dinitrobenzene is decomposed when boiled with potash or soda solution, with production of hydrocyanic acid, and that mononitrobenzene is similarly acted upon when brought into contact for a short time with potassium hydrate heated to fusion. No other special products of this decomposition besides hydrocyanic acid were observed. The authors mean to extend the investigation to as many nitro- and amido-compounds as possible.

E. D.

**Formation of Azobenzene.** By AD. CLAUS (Deut. Chem. Ges. Ber., v, 364—367).

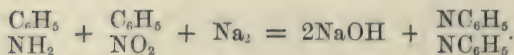
THE preparation of azobenzene is best effected by a modification of the process originated by Mitscherlich. One part of sodic hydrate is dissolved in 5·6 parts of alcohol, heated to boiling in a flask with inverted condenser, and 2 parts of nitrobenzene are then added by degrees. The best results are then obtained by distilling off the greater part of the alcohol, saturating with dilute hydrochloric acid, and, after the addition of chlorine-water, shaking up with light benzene.

The azoxybenzene remaining after removal of the benzene is not quite pure, but the tarry compounds mixed with it are in very small quantity if the necessary amount of chlorine-water has been employed.

Large quantities of azoxybenzene cannot be transformed into azobenzene by simple distillation, for at a certain point the temperature suddenly rises, a violent reaction sets in, and the whole is converted into a carbonaceous mass. This spontaneous decomposition may be avoided, however, by mixing the azoxybenzene with twice its weight of common salt. The distillation then proceeds uniformly and quietly, and a satisfactory yield of azobenzene is obtained.

Some experiments were undertaken with the intention of effecting the reduction of the nitrobenzene by means of the hydrogen of the amidogen group in aniline, but it was found that aniline and nitrobenzene, heated together to 250°, even in presence of dehydrating agents, exerted no action upon each other. Azobenzene was obtained, however, when aniline and nitrobenzene, dissolved in benzene, were acted upon by sodium amalgam:





The process, however, is not very productive. The author intends, in conjunction with Dr. Rasenack, to operate on a mixture of toluidine and nitrobenzene with the view of obtaining a mixed azo-compound.

Lastly, the action of sodium upon nitrobenzene was investigated.

Perfectly anhydrous nitrobenzene is not attacked by sodium amalgam, or by sodium, which only becomes covered with a brown film, but when water is added drop by drop a reaction soon commences, and azobenzene is formed. The reduction takes place more readily when nitrobenzene is dissolved in ether containing water, and this medium possesses over alcohol the additional advantage that the sodium hydrate, which is formed, is not dissolved. At the end of the reaction the ethereal solution is poured or filtered off, and pure azobenzene, amounting to 80 per cent. of the theoretical yield, is obtained.

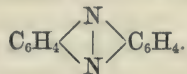
W. A. T.

**Azophenylene, a New Nitrogenous Compound of the Aromatic Series.** By AD. CLAUS (Deut. Chem. Ges. Ber., v, 367—370).

AZOBENZOIC acid, according to general opinion, stands in the same relation to azobenzene that benzoic acid does to benzene. The distillation of calcium azobenzoate with lime does not, however, yield azobenzene, but a red oil which after a time becomes crystalline. This is a mixture of azophenylene, the new compound, with another body which has not yet been examined.

Sublimed azophenylene forms inch-long, fine, pale-yellow, shining needles, which melt at 170°—171°, and sublime at a higher temperature. It is very slightly soluble in hot water, but may easily be volatilised with aqueous vapour, by which it is obtained in small needles, almost colourless. It is soluble in fifty parts of cold alcohol, easily in hot alcohol, and also to some extent in ether and benzene. A nitro-derivative appears to be formed by the action of concentrated nitric acid.

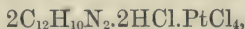
The formula of azophenylene is  $\text{C}_{12}\text{H}_8\text{N}_2$ , or



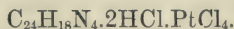
It combines directly with bromine to form the compound  $\text{C}_{12}\text{H}_8\text{N}_2\text{Br}_2$ . It also unites with hydrogen, giving rise to hydrazophenylene,  $\text{C}_{12}\text{H}_{10}\text{N}_2$ .

This compound is obtained by the action of hydrogen sulphide on an ammoniacal solution of azophenylene in alcohol. In some experiments an intermediate compound, forming deep blue needles, was observed.

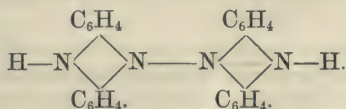
Hydrazophenylene is almost insoluble in water and benzene, and is taken up by cold alcohol in small quantity only. At about 200° it gives off hydrogen, and is retransformed into azophenylene, the formation of the blue intermediate product being again observable. Boiled with dilute acids, it dissolves and forms salts of a green colour, but which are not of constant composition. A double platinum salt has been obtained—



or perhaps—



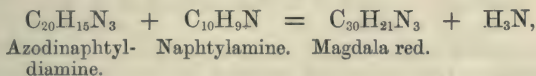
On the whole it seems probable that hydrazophenylene does not itself possess the properties of a base, but that a base is formed from it by the action of acids, probably by union of two molecules, with loss of two atoms of hydrogen—



W. A. T.

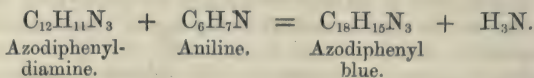
**On Colouring Matters derived from the Aromatic Azodiamines.** By A. W. HOFMANN and A. GEYGER (*Deut. Chem. Ges. Ber.*, v, 472—476).

ONE of the authors (Hofmann, *Deut. Chem. Ges. Ber.*, ii, 374 and 412) has already shown that the so-called “Magdala red” of commerce is formed by the action of naphthylamine on azodinaphtyldiamine, with simultaneous elimination of ammonia,



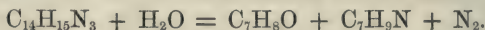
and it seemed probable that the blue compound produced by the action of azodiphenyldiamine on aniline salts, and described by Martius and Griess (*Monatsber. der Akad.*, 1865, 640), belonged to the same class. The author, prepared this *azodiphenyl blue* by heating equal weights of the azo-base and aniline hydrochloride with twice the weight of alcohol to 160° for four or five hours. The product was treated with boiling water, the residue dissolved in alcohol with the aid of hydrochloric acid, and precipitated again by soda. On dissolving the base in alcohol, adding hydrochloric acid, and concentrating the solution, a dark blue crystalline salt was obtained. This is insoluble in water and in ether, but readily soluble in alcohol, especially when warm. The solution, which is of a deep violet-blue colour, dyes wool and silk. It is decolorised by zinc and hydrochloric acid, but no corresponding leuko base could be isolated. Soda precipitates the base from the concentrated alcoholic solution of its salts as a dark brown powder, which is insoluble in water, but soluble in alcohol or ether; the addition of hydro-

chloric acid to the latter solution precipitates the base as hydrochloride. The formation of azodiphenyl blue may be represented thus:—



The *hydrochloride* has the composition,  $\text{C}_{18}\text{H}_{15}\text{N}_3 \cdot \text{HCl}$ , but loses part of its acid on being dried at a high temperature, or by recrystallisation from alcohol. The *hydriodide*,  $\text{C}_{18}\text{H}_{15}\text{N}_3 \cdot \text{HI}$ , is very similar to the hydrochloride in its properties. The *picrate*,  $\text{C}_{18}\text{H}_{15}\text{N}_3 \cdot \text{C}_6\text{H}_3(\text{NO}_2)_3\text{O}$ , forms a blue powder, quite insoluble either in water or in ether, and only very sparingly soluble in boiling alcohol. The authors notice that this azodiphenyl blue has the same composition as the *violanine*,  $\text{C}_{18}\text{H}_{15}\text{N}_3$ , obtained by Girard, De Laire, and Chapoteaud (Compt. rend., lxxiii, 964) by the oxidation of pure aniline,  $3\text{C}_6\text{H}_7\text{N} - 3\text{H}_2 = \text{C}_{18}\text{H}_{15}\text{N}_3$ , but they have not, as yet, had an opportunity of ascertaining whether the two are identical.

Blue colouring matters, very similar to the azodiphenyl blue, are produced by the action of toluidine or naphthylamine hydrochloride on azodiphenyldiamine. These most likely have the composition,  $\text{C}_{19}\text{H}_{17}\text{N}_3$  and  $\text{C}_{22}\text{H}_{17}\text{N}_3$ , and it seemed highly probable that azoditolyldiamine would produce similar compounds. In their endeavours to prepare azoditolyldiamine, however, the authors were as unsuccessful as Martius had been. On passing a rapid stream of nitrous acid through fused toluidine, floating on a hot saturated solution of common salt, the base gradually solidifies to a crystalline mass, which, when purified by recrystallisation from alcohol, forms dark yellow needles of diazoamidotoluene,  $\text{C}_{14}\text{H}_{15}\text{N}_3$ , the isomeride of azoditolyldiamine; on boiling this with hydrochloric acid, it splits up into cresol and toluidine with evolution of nitrogen:



The action of this compound on aniline, toluidine, and naphthylamine hydrochlorides produces colouring matters, but the bye-products formed at the same time show that the reaction is a very complex one.

C. E. G.

**On Bromotoluenes.** By H. HUEBNER and G. RETSCHY (Zeitschr. f. Chem., vii, 618—631).

THE authors have carefully re-examined the two isomeric bromotoluenes, which are found simultaneously by the direct action of bromine upon toluene.

*Parabromotoluene*.—By repeated recrystallisation from alcohol, this compound was obtained in splendid crystals, melting at  $28^\circ$ — $29^\circ$ , and solidifying again at  $28^\circ$ ; it boils constantly at  $185.2^\circ$ . On dissolving it in 3—4 vols of fuming sulphuric acid at a temperature not exceeding  $80^\circ$ , two isomeric sulpho-acids are formed, which were separated in the form of barium salts.

*Orthobromotoluene*.—The crude compound forming about one-half of the total product was cooled down to  $-20^\circ$ . On adding a few pieces of



calcium chloride some crystals of the para-compound separated. The liquid was poured off and twice cooled down for some hours to  $-21^{\circ}$ , when some more of the solid compound crystallised out. After seven fractional distillations, the liquid boiled at  $183.2^{\circ}$ , but it still contained a little of the para-compound, which was removed by acting on the liquid bromotoluene with a mixture of manganese dioxide, sulphuric acid, and glacial acetic acid, the parabromotoluene being oxidised to parabromobenzoic acid, whilst a part of the orthobromotoluene was completely destroyed, resembling in this respect orthonitrotoluene, which, like the bromo-compounds, does not give on oxidation a substituted benzoic acid.

Pure orthobromotoluene is a limpid liquid, boiling at  $181^{\circ}$ — $182^{\circ}$ , which is not acted upon by sodium in the cold.

On dissolving it at a gentle heat in Nordhausen sulphuric acid, it yields only *one sulpho-acid*.

The following table contains the derivatives of the two bromotoluenes examined by the authors. For comparison the derivatives of meta-bromotoluene are also added.

Parabromotoluene solid, melting-point, $28.5^{\circ}$ , boiling-point, $185.2^{\circ}$ .	Metabromotoluene, from acetbromotoluidine liquid, boiling-point, $182^{\circ}$ . Wroblevsky.	Orthobromo- toluene liquid, boiling-point, $181^{\circ}$ .
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$\alpha$ -series.	$\beta$ -series.	$\alpha$ -series.	$\beta$ -series.	$\gamma$ -series.	$\alpha$ -series.
$\text{A}_2\text{Ba} + 7\text{H}_2\text{O}$	$\text{A}_2\text{Ba} + \text{H}_2\text{O}$	$\text{A}_2\text{Ba} + \text{H}_2\text{O}$	$\text{A}_2\text{Pb} + \frac{1}{2}\text{H}_2\text{O}$	$\text{A}_2\text{Ba} + 2\frac{1}{2}\text{H}_2\text{O}$	$\text{A}_2\text{Ba} + 2\text{H}_2\text{O}$
$\text{A}_2\text{Pb} + 3\text{H}_2\text{O}$	$\text{A}_2\text{Pb} + 3\text{H}_2\text{O}$	—	$\text{A}_2\text{Pb} + 3\text{H}_2\text{O}$	—	$\text{A}_2\text{Pb} + 2\text{H}_2\text{O}$
$\text{A}_2\text{Sr} + 7\text{H}_2\text{O}$	—	—	—	—	—
—	$\text{A}_2\text{Ca} + 4\text{H}_2\text{O}$	—	$\text{A}_2\text{Ca} + 2\frac{1}{2}\text{H}_2\text{O}$	—	$\text{A}_2\text{Ca}$

*Bromotoluene-sulphamides*,  $\text{C}_6\text{H}_3.\text{CH}_3.\text{Br}.\text{SO}_2.\text{NH}_2$ .

Melting-point, $151.5^{\circ}$ .	$166.5^{\circ}$ .	—	$133.5^{\circ}$ .
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*Bromobenzoic acids*,  $\text{C}_6\text{H}_4.\text{Br}.\text{COOH}$ .

Melting-point, $251^{\circ}$ .	$155^{\circ}$ .	$137^{\circ}$ .
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The most characteristic derivatives of the two bromotoluenes are the barium salts of their sulpho-acids. These have already been examined by one of the authors, in conjunction with Post; from the results of this examination they concluded that parabromotoluene yielded three sulpho-acids; but Huebner and Retschy find now that only two exist, the cause of the former mistake being that the salt of the  $\beta$ -acid crystal-

lises under different conditions in two distinct forms, but of the same composition.

1. *Para-acid*.  $\alpha(\text{C}_6\text{H}_3\cdot\text{CH}_3\cdot\text{Br}\cdot\text{SO}_3)_2\text{Ba} + 7\text{H}_2\text{O}$ , crystallises in long, thick, well-formed needles, which remain transparent when exposed to the sunlight.

$\beta(\text{C}_6\text{H}_3\cdot\text{CH}_3\cdot\text{Br}\cdot\text{SO}_3)_2\text{Ba} + \text{H}_2\text{O}$ , separates from a cold saturated solution on spontaneous evaporation in hard, thick crystals, apparently consisting of rhombic tables grouped in rosettes. From a hot supersaturated solution it separates as an apparently amorphous powder, which, when dissolved in a larger quantity of hot water, crystallises on slowly cooling in large, thin, flexible plates, assuming a silky lustre when dry.

2. *Ortho-acid*.  $(\text{C}_6\text{H}_3\cdot\text{CH}_3\cdot\text{Br}\cdot\text{SO}_3)_2\text{Ba} + 2\text{H}_2\text{O}$ ,\* crystallises in large, thin, brilliant, elongated tables; one part dissolves in 253 parts of water at  $17^\circ$ . This salt is most readily obtained in a pure state, and is identical with that obtained by Mueller from crude liquid bromotoluene (*Zeitschr.*, 1870, 450), and that which Post prepared from an impure solid bromotoluene.

In order to see whether, under the influence of heat, one sulpho-acid might be converted into another, or new isomeric modification, some pure  $\beta$ -parabromotoluene-sulphonic acid was heated to  $185^\circ$  during six hours, and then a part converted into the amide, and another into the barium salt; but no change had taken place, the compounds obtained being identical with those prepared from the non-heated acid.

C. S.

**Dibromotoluene.** By E. WROBLEVSKY (*Zeitschr. f. Chem.*, vii, 609).

By treating orthoacetoluide with bromine, and decomposing the brominated toluidine with potash, *metabromorthotoluidine* was obtained, a liquid boiling at  $240^\circ$ , and smelling like toluidine. The nitrate was converted into the diazo-compound, the perbromide of which yielded, by decomposing it with absolute alcohol, a *dibromotoluene* crystallising in needles, melting at  $42.5^\circ$ , and boiling at  $249^\circ$ . It is identical with the dibromotoluene formed by removing the amido group from dibromometatoluidine.

*Metabromotoluene* is obtained by the same reaction from metatoluidine; it is a liquid boiling at  $182^\circ$ — $183^\circ$ , and not solidifying even at  $-20^\circ$ .

C. S.

**Naphthalene Derivatives.** By J. BATTERSHALL (*Zeitschr. f. Chem.* [2], vii, 673).

NAPHTHOIC aldehyde has been described in this Journal (1871, 1057). Further experiments, however, indicate that the substance thus

\* According to the table, this salt contains 2 molecules of water; but on describing it, the authors give to it only 1 molecule. The former statement appears, however, to be the right one, as the authors say that it differs by the water of crystallisation from all the salts of the two other acids.

operated on was not pure naphthoic acid. The pure acid gives no aldehyde at all, or only traces, on distillation of its calcium salt with calcium formate. Isonaphthoic acid, on the other hand, yields a finely crystallised aldehyde, melting constantly at  $59.5^{\circ}$ . This forms a crystalline compound with sodium bisulphite, and yields pure isonaphthoic acid, melting at  $182^{\circ}$ , by oxidation with potassium permanganate. When a naphthoic acid containing small quantities of isonaphthoic acid is employed, a liquid distillate is obtained, from which crystals (of isonaphthoic aldehyde?) separate on standing; and the acid obtained by oxidation of the liquid aldehyde shows no constant boiling-point; *both* acids apparently take part in the reaction in this case. The author finds that the difference in solubility of the calcium salts of naphthoic and isonaphthoic acids affords a better means of separating them than Merz's method, by means of the sulpho-acids.

Nitric acid converts isonaphthoic aldehyde into a crystalline, not acid compound, which is converted into difficultly purifiable, non-crystalline substances by nascent hydrogen. Alcoholic ammonia dissolves the aldehyde; on standing for some days, the whole becomes converted into *hydro-isonaphthamide*,  $(C_{10}H_7.CH)_3N_2$ , analogous in composition to hydrobenzamide. This is insoluble in water, cold alcohol, and ether, and melts at  $146^{\circ}$ — $150^{\circ}$ . Boiling water has no action on it; but boiling alcohol slowly converts it into isonaphthoic aldehyde and ammonia. Diluted hydrochloric acid produces the same reaction on gently warming.

Fuming sulphuric acid converts naphthoic acid into a mixture of at least two sulpho-acids, each consisting of  $C_{10}H_6 \begin{cases} CO.OH \\ SO_2.OH \end{cases}$ . Both furnish crystallisable barium salts, of which one crystallises first from the mixture of salts obtained on neutralising the crude acids with barium carbonate. This barium salt is  $C_{10}H_6 \begin{cases} CO.O \\ SO_2.O \end{cases} Ba + 4H_2O$ , and furnishes an acid ( *$\alpha$ -sulphonaphthoic acid*) readily soluble in water, crystallisable in colourless needles, and melting at  $230^{\circ}$ — $240^{\circ}$  with slight decomposition.

C. R. A. W.

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**On Nitronaphthalenes.** By A. A. DE AGUIAR (Deut. Chem. Ges. Ber., v, 370).

At least seven distinct nitro-compounds are producible by the action of nitric acid on naphthalene, and are separable with more or less difficulty by fractional crystallisation, glacial acetic acid serving better as a solvent than ethylic or methylic alcohol, benzene, or chloroform.

*Mononitronaphthalene* is best prepared by treating naphthalene, dissolved in boiling glacial acid, with ordinary nitric acid, and boiling for half an hour. No red vapours are evolved, and on cooling, the whole becomes a mass of crystals, which are perfectly pure after one crystallisation from alcohol. The author finds that the pure body melts at  $61^{\circ}$ , some degrees higher than the melting point found by previous chemists.

*Dinitronaphthalene*.—Fuming nitric acid and naphthalene, boiled



together for some hours, yield two modifications,  $\alpha$  and  $\beta$ , in nearly equal quantities. On cooling, a crystalline mass separates, usually containing only traces of trinitronaphthalene. This mass is washed and dried, and then boiled with glacial acetic acid (about  $2\frac{3}{4}$  times its weight). Pure  $\alpha$  dinitronaphthalene remains undissolved, and may be crystallised from a large quantity of fresh acid. The  $\beta$  modification is much more soluble than the  $\alpha$ , and is readily obtained pure by a few fractional crystallisations of the product obtained from the dissolved part. The two bodies differ in their crystalline forms and melting points, the  $\alpha$  body melting at  $216^\circ$ , and the  $\beta$  at  $170^\circ$ . A small quantity of what appears to be a third modification is also obtained, but cannot readily be purified, as its solubility is nearly the same as that of  $\beta$ -dinitronaphthalene.

*Trinitronaphthalene.*—Two modifications of this derivative exist, obtainable by the action of nitric acid on naphthalene; their separation and purification is, however, difficult. Much better results are obtained by nitrating  $\alpha$ - and  $\beta$ -dinitronaphthalene in sealed tubes at  $120^\circ$ — $130^\circ$ , or in a retort with inverted condenser.  $\alpha$ -dinitronaphthalene, thus treated, gives a product which, after precipitation by water and crystallisation from alcohol, benzene, glacial acetic acid, or chloroform (the last being the best), yields fine crystals of  $\alpha$ -trinitronaphthalene, melting at  $122^\circ$ , and solidifying at  $90^\circ$ .  $\beta$ -dinitronaphthalene similarly yields  $\beta$ -trinitronaphthalene, melting at  $218^\circ$ ; the latter trinitro body is much less soluble in alcohol and chloroform than the former, but is crystallisable from these media.

*Tetranitronaphthalene.*—If the action of the nitric acid in preparing trinitronaphthalene be carried on for two days, tetranitrated bodies are formed. The one from  $\alpha$ -dinitronaphthalene is termed  $\alpha$ -tetranitronaphthalene, and is almost insoluble in alcohol. From acetic acid it cannot be crystallised; but from chloroform readily, the crystals melting at  $259^\circ$ , and solidifying at  $225^\circ$ .  $\beta$ -tetranitronaphthalene melts at  $200^\circ$ .

$\alpha$ -trinitronaphthalene and  $\alpha$ -tetranitronaphthalene are new derivatives, the others having been previously known.

C. R. A. W.

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### Conversion of Ethylene-naphthalene into Acenaphthene. By BERTHELOT and BARDY (Compt. rend., lxxiv, 1463—1465).

ETHYLENE-NAPHTHALENE,  $C_2H_4.C_{10}H_8$ , obtained from brominated naphthalene by ethyl iodide and sodium, can be converted into acenaphthene,  $C_{12}H_8$ , a synthetic product of naphthalene with acetylene, (*Ann. Chim. Phys.* [4], xii, 181, by passing it through a porcelain tube at a bright red heat, when naphthalene and acenaphthene are produced, and may be separated by fractional distillation. The change may be also effected in the wet way by heating ethylene-naphthalene to  $180^\circ$  with two equivalents of bromine, treating the crude liquid (which cannot be purified by distillation) with alcoholic potash at  $100^\circ$ , and at the end of twelve hours pouring the mother-liquor into water. The heavy oily layer which separates is distilled, and the portion passing over at  $300^\circ$  is treated with alcoholic picric acid. The red precipitate,

decomposed by ammonia, gives a liquid which deposits acenaphthene in crystals.

C. G. S.

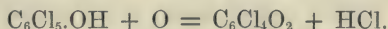
**Perchlorophenol.** By V. MERZ and W. WEITH (Deut. Chem. Ges. Ber., v, 458—463).

THIS body is readily obtained by the action of chlorine upon a mixture of phenol and antimony chloride. The crude product is purified by distillation with steam at  $180^{\circ}$ — $200^{\circ}$ . It crystallises from petroleum-naphtha in thin long brilliant needles. At the common temperature it is odourless, but when heated it gives off a very pungent odour, producing coughing. It melts at  $186^{\circ}$ — $187^{\circ}$ , and can be sublimed by heating it carefully; but it boils only at a very high temperature, with partial decomposition. It dissolves slowly in cold solution of sodium and potassium carbonates, and is precipitated again by passing carbon dioxide in the very dilute solutions.

*Potassium perchlorophenylate*,  $C_6Cl_5OK$ , crystallises from a mixture of ether and alcohol in long, white needles, and from concentrated potash-solution in fasciculated prisms, with diamond lustre. The sodium compound is a very similar body. *Ammonium perchlorophenylate*,  $C_6Cl_5ONH_4$ , crystallises from hot ammonia in very long, thin, and flexible needles. It is soluble in alcohol, but so sparingly soluble in water that even dilute solutions of ammonium chloride are precipitated by chlorophenylates.

Sodium-amalgam and water act but slowly on perchlorophenol; even after some weeks the product still contained chlorine, consisting principally of monochlorophenol.

Perchlorophenol is soluble in hot concentrated sulphuric acid, and is completely destroyed on heating the solution more strongly, without any sulpho-acid being formed. Cold concentrated nitric acid converts it into chloranil—

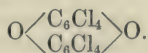


Hot nitric acid attacks it violently, forming, besides chloranil, a considerable quantity of chloropicrin. By distilling perchlorophenol with phosphorus pentachloride, perchlorobenzene is produced.

When perchlorophenol is boiled as long as hydrochloric acid is given off, and the residue, mixed with sand, is heated in a combustion-tube, or when the potassium compound is heated in such a tube, the following reaction takes place:—



As the *perchlorophenylene oxide* thus produced has a very high boiling point, it has probably the following constitution:—



It is almost insoluble in alcohol, ether, chloroform, carbon disulphide, &c., but is very freely soluble in boiling nitrobenzene, less so in

hot turpentine-oil, and crystallises from these solutions in broad needles resembling benzoic acid. At the common temperature it is odourless, but when heated it gives off a penetrating, pungent, and acrid odour. It melts at about  $320^{\circ}$ , and sublimes in long needles, but boils only above the boiling-point of mercury. It is not acted upon by sodium-amalgam and water, or by phosphorus pentachloride, even at  $250^{\circ}$ . Boiling concentrated nitric acid destroys it slowly, with evolution of carbon dioxide and chlorine.

Caustic potash attacks perchlorophenol only slowly below  $200^{\circ}$ , and at  $230^{\circ}$ — $240^{\circ}$  it is converted partially in humus-like bodies, which contain no chlorine, and are insoluble in water and potash-solution. A considerable quantity of oxalic acid is likewise produced.

These experiments were tried for the purpose of replacing chlorine by hydroxyl. As the desired result could not be obtained, chloranilic acid was tried. By fusing it with caustic potash, at  $150^{\circ}$ — $170^{\circ}$ , in a current of hydrogen, considerable quantities of oxalic acid and potassium chloride were produced, and by heating potassium chloranilate with potassium acetate and water to  $170^{\circ}$ , or with water alone, the following reaction takes place:—



When the dry salt is heated rapidly, it decomposes with a slight explosion below  $200^{\circ}$ , and when it is slowly heated above  $250^{\circ}$ , clouds of carbon and carbon dioxide are given off.

C. S.

**Benzylated Phenol.** By E. PATERNO (*Gazzetta Chimica Italiana*, ii, 1—6).

THE author has already shown (this vol., 241, and *Gaz. Chim. Ital.*, i, 589), that the action of benzol chloride on anisol in the presence of zinc, produces a compound,  $\text{CH}_2\text{C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_5\text{OCH}_3$ , which may be regarded as the methylic ether of a new phenol.

1. *Benzylated Phenol.*—When a mixture of benzyl chloride and phenol is gently heated with metallic zinc, hydrochloric acid is evolved in abundance, and the liquid in a short time enters into ebullition. As soon as the action has ceased, the brown liquid is separated from the zinc and distilled under the ordinary pressure. Unaltered phenol and benzyl chloride pass over below  $260^{\circ}$ , leaving the new phenol in the retort. On distilling this residue under diminished pressure (6 mm.), most of it passes over between  $180^{\circ}$  and  $190^{\circ}$ , and solidifies, on cooling, to a crystalline mass, consisting of small needles, contaminated, however, with an oil, which may be removed by pressure and subsequent crystallisation from alcohol. The yield is about 15 per cent. of the phenol originally employed. Pure benzylated phenol,  $\text{C}_{13}\text{H}_{12}\text{O}$ , as thus obtained, crystallises in white silky needles or lustrous plates, which are not altered by exposure to the air, and are soluble in alcohol, ether, benzene, and chloroform. It melts at  $84^{\circ}$ , and distils under a pressure of 4 or 5 mm. at  $175^{\circ}$  to  $180^{\circ}$ . It dissolves in alkaline solutions, and is precipitated again by acids,



but is insoluble in ammonia. With nitric acid it gives substitution-products, and with sulphuric acid a sulphonic acid, the barium salt of which is soluble in water. The potassium salt, when fused with potassium hydrate, yields a crystalline compound, which is probably a new diatomic phenol,  $C_{13}H_{10}(OH)_2$ . The author is engaged in the examination of the substance, as well as of the secondary products formed during the action of zinc on the mixture of phenol and benzyl chloride.

2. *Benzylated Anisol*,  $C_{13}H_{14}O$ .—This compound, prepared, as already stated, by the action of zinc on a mixture of anisol and benzyl chloride, after separation from the excess of zinc, is first purified by distilling off the portion below  $250^\circ$ . This contains the benzyl chloride and anisol, and the residue, consisting of the impure benzylated anisol, is then submitted to repeated fractional distillation under diminished pressure. The pure substance is a colourless, mobile liquid, which does not solidify, even at a very low temperature, and boils at about  $305^\circ$  under the ordinary pressure at  $170^\circ$ , under a pressure of 10 mm., and at  $155^\circ$  under a pressure of 4 mm. It has an aromatic odour, recalling that of anisol, and a high refractive power. In this reaction another oily compound is formed, boiling at  $200^\circ$  under a pressure of 9 mm., and which the author believes to be the methylic ether of a phenol.

3. *Action of Hydriodic Acid on Benzylated Anisol*.—On heating the benzylated anisol with hydriodic acid to  $170^\circ$  for eight hours, it was found to be decomposed, yielding methyl iodide and a colourless crystalline substance. The latter, when purified, melted at  $84^\circ$ , and agreed in all other respects with the benzylated phenol prepared directly from benzyl chloride and phenol.

C. E. G.

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**The Effect of active Oxygen upon Pyrogallie Acid.** By  
H. STRUVE (Ann. Chem. Pharm., cxliii, 163—174).

THE author finds that pyrogallie acid is as sensitive to the oxidizing action, not only of metallic peroxides, but to that of many organic substances in the presence of oxygen, as guaiacum. Purpurogallin, the substance obtained by Girard (*Compt. rend.*, lxi, 865) from pyrogallie acid by the action of silver nitrate, or of potassium permanganate and sulphuric acid, is the principal product of the oxidation effected by lead peroxide, hydrogen peroxide, ozonized oil of turpentine, blood, saliva, gum, and extract of malt (prepared according to the directions of Schönbein for use as a test of the presence of minute quantities of hydrogen peroxide). It is quite as sensitive to the action of these substances as guaiacum. The statement of Schönbein that hydrogen peroxide is not acted upon by pyrogallie acid, and that it is formed during the oxidation of the latter, is not correct. During the oxidation of pyrogallie acid in presence of alkalis, or of gum, however, ozone is formed in the air over the solution. Schönbein's statement that ozonised oil of turpentine does not give up its active oxygen to pyrogallie acid, is likewise incorrect; it does so most completely.

Alkalis and most metallic peroxides exert a too energetic influence upon pyrogallie acid for the process of the oxidation to be followed out,

and the formation of purpurogallin to be observed. Cane sugar, grape sugar, starch, urine, and pepsin do not cause the oxidation of pyrogallie acid. The author is uncertain about albumin and gelatin. Pyrogallie acid in solution is converted, very slowly but spontaneously, into purpurogallie acid, but not to any extent.

For the purpose of detecting the presence of purpurogallin, which is insoluble in water, the author avails himself of the blue colour which the substance, when pure, strikes with alkalis, and the appearance of its hair-like crystals under the microscope. These occur in tufts terminating in cup-shaped expansions, and have the colour and lustre of bronze. Purpurogallin, like pyrogallie acid, gives Trommer's re-action with cupric sulphate and an alkali.

Gum is the best substance to employ in the production of purpurogallin. When dropped in fragments into a solution of pyrogallie acid, it acts too intensely. The production of purpurogallin is best observed by taking 50 c.c. of solution containing 1 per cent. of gum, and adding 0.2 per cent. of pyrogallie acid, which immediately dissolves, and almost at once communicates a yellowish colour to the solution. The solution gradually becomes more coloured, and in a few hours the formation of the crystals of purpurogallin is evident to the naked eye. They appear first at the surface of the solution, then on the sides of the vessel, and lastly at the bottom. By frequently shaking the solution with air, the formation of the purpurogallin is hastened. It must be washed with water before it is treated with ammonia or other alkali, in order to obtain the blue colour.

The author believes the action of extract of malt to be due to the gum which it contains. Gum, which has been purified by Neubauer's hydrochloric acid process, fails, even after all hydrochloric acid has been removed, to act upon pyrogallie acid, and the two may be kept together for a long time with scarcely any change. When the solution becomes mouldy, some purpurogallin forms between the filaments of the fungus. From this the author concludes that the setting up of the process of oxidation is secondary to that of the process of vegetation. Treatment of gum with acetic acid does not destroy its activity towards either pyrogallie acid or guaiacum. Boiling the solution of gum also does not destroy its activity, but causes its effects upon both pyrogallie acid and guaiacum to be produced more slowly.

The author considers that gum performs a similar function in the vegetable kingdom to that performed by blood in the animal kingdom, that is, that it serves as a carrier of oxygen.

When 2 c.c. of fresh blood are mixed with 200 c.c. of water, and 0.5 per cent. of pyrogallie acid added, a light, amorphous precipitate is produced; in a few moments the solution becomes gradually dark-coloured, and in 24 hours a considerable quantity of purpurogallin has separated, more especially if the solution has been frequently agitated. On filtering the solution and washing the precipitate, the first washings give a dirty brown colour with ammonia, but the after portions give the blue colour. The residue on the filter, treated with acetic acid and sal-ammoniac, gives, on evaporation, most beautiful hæmin crystals. Fresh blood is more sensitive than old to pyrogallie acid.

E. D.

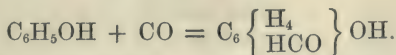


**Corallin.** By H. FRESSENIUS (J. pr. Chem [2], v, 184—206).

THE author has obtained in well-formed crystals both the substance formed by Kolbe and Schmitt's process of treating phenol with sulphuric acid and oxalic acid, and that formed by Caro and Wanklyn's process of treating rosaniline with nitrous acid, and found them to be different bodies.

The essential part of the process of purifying the former substance consisted in combining it with magnesia, and afterwards decomposing the compound with sal-ammoniac. Crystallised from alcohol it forms filamentous, interlacing, scarlet, lustrous crystals; crystallised from glacial acetic acid, it forms magnificent prisms, red by transmitted, dark-green by reflected light, measurements of which by P. Groth are given in the paper. It is tolerably soluble in phenol, to a small extent in boiling chloroform and boiling benzene, and not at all in carbon bisulphide. Its melting point is  $156^{\circ}$ . The author believes that Kolbe and Schmitt found the melting point to be  $80^{\circ}$ , in consequence of the corallin examined by them containing considerable quantities of phenol. He believes the substance examined by Dale and Schorlemmer (*Chem. Soc. J.* [2], x, 74), which can be heated to  $200^{\circ}$ , without melting, and has the composition  $C_{20}H_{14}O_3$ , to be a different body. The impure corallin dissolved in an alkali becomes darker in colour when treated with potassium ferricyanide. As an alkaline solution of phenol is rendered of a dark colour by this reagent, the author attributes the darkening of the impure corallin to the presence of this body, and not to leucocorallin, as suggested by Caro and Wanklyn.

The author deduces from his analyses the formula,  $C_{40}H_{38}O_{11}$ ; but he has ascertained that the gas which escapes during its preparation by oxalic acid is principally carbon dioxide; that therefore it is the nascent carbon monoxide from the oxalic acid which is the active substance in its formation; and that, in confirmation of this conclusion, formic acid may be substituted for the oxalic acid, with production of apparently the same colouring matter. These observations have caused Kolbe to suggest, in a note to the author's paper, that corallin is formylated phenol, having the formula  $C_7H_6O_2$ , the calculated numbers for which agree very well with the numbers obtained. Its formation on this view may be represented thus:—



When either phenetol or anisol is substituted for phenol, the author finds that corallin is still obtained, judging from its properties and composition in the crude state. The preparation of corallin also proceeds equally well, whether the phenolsulphonic acid acted upon by the oxalic acid is the meta or the para variety.

The author proposes to call Caro and Wanklyn's rosolic acid pseudo-corallin. In the crystalline state it resembles corallin crystallised from alcohol, and is also like it in other of its properties. But its composition is expressed by the formula,  $C_{26}H_{28}O_{10}$ ; its melting point is about



158°, and, unlike corallin, its alcoholic solution is not decolorised by a concentrated solution of acid sodium sulphite. Caro and Wanklyn, from synthetical experiments, ascribed to it the formula,  $C_{20}H_{16}O_3$ .

E. D.

**Colouring Matter of Cochineal.** By C. LIEBERMANN and W. A. VAN DORP (Ann. Chem. Pharm., clxiii., 97—120).

THE first part of this paper relates to nitrococcusic acid, trinitro-cresol, and ruficoccin, an account of which has already appeared in this Journal [2], ix, 912. The authors have re-examined ruficoccin, which is a compound produced by heating carmine with concentrated sulphuric acid. They find, according to more recent analyses, that the formula of this body should be  $C_{16}H_{10}O_6$ , not  $C_{16}H_{12}O_6$ , as given in their former paper. It yields a calcium compound,  $C_{16}H_8CaO_6$ , but they have been unable to obtain a definite acetyl derivative.

By heating ruficoccin with zinc-dust, a solid crystalline hydrocarbon is obtained, which sublimes in white plates, with a melting point varying between 183° and 188°. Its formula is  $C_{16}H_{12}$ . It furnishes by oxidation a quinone, which melts at 250°. Anthraquinone, which it much resembles, melts at 275°.

Another body formed at the same time as ruficoccin, by the action of sulphuric acid on carmine, appears to have the formula,  $C_{32}H_{20}O_{13}$ , and inasmuch as it yields, after heating with baryta-water, the same hydrocarbon as ruficoccin, it appears to contain the same carbon nucleus.

By heating carmine with water to 200°, a dark resinous body was deposited, from which ether extracted a carmine-red powder, which differed from carmine-red by its total insolubility in water, and from ruficoccin by its extreme solubility in alcohol. This body, which the authors call *ruficarmin*, is another product of the condensation of carmine-red, and possesses the formula,  $C_{16}H_{12}O_6$ .

Although there is evidently a close connection between ruficoccin and ruficarmin, and the coccinin,  $C_{16}H_{16}O_6$ , of Hlasiwetz and Grabowski, attempts to obtain coccinin from these two bodies by reduction with sodium-amalgam, or by fusion with alkali, have not been successful.

W. A. T.

**Chinese Green (Lokao).** By S. CLOEZ and E. GUIGNET (Bull. Soc. Chim. de Paris, xvii., 247—253).

ALTHOUGH, for the dyer, Chinese green has lost much of its value since the introduction of the aniline colours, its chemical and tinctorial properties are well worth studying, as the following commencement of a research will show.

The crude lokao is a lake containing 25 per cent. of mineral matter. If left in contact with water for some days, it ferments, and is partially reduced. The liquor is filtered, and the residue washed with cold

water, and dissolved in warm water, which it colours a reddish-violet. This solution, on exposure to air, throws down a blue precipitate, which, though purer than the original lokao, still leaves a considerable ash on ignition. Perfectly pure lokao is obtained by agitating the crude green with solution of ammonia carbonate, filtering, precipitating with alcohol, washing, and drying at  $100^{\circ}$ . The product is blue (confirming the observation of Persoz, that "Chinese green, when quite pure, is a blue"), and is a compound of ammonia with the pure colouring matter (*lokaïn*). The analysis of ammonium-lokaïn gives numbers corresponding to the formula,  $(\text{NH}_4)_2\text{C}_{56}\text{H}_{66}\text{O}_{34}$ . Lokaïn may be considered as a weak acid, and represented by the formula,  $\text{C}_{56}\text{H}_{66}\text{O}_{34}$ .

When ammonium-lokaïn is kept at  $100^{\circ}$  for some hours, it is transformed into an insoluble violet substance, which is also formed when crude lokao is fermented with yeast, but is best obtained by treating ammonium-lokaïn with warm dilute sulphuric acid, when it splits up into glucose (showing that lokaïn is a glucoside), and an insoluble residue (*lokaëtin*), the composition of which may be expressed by the formula,  $\text{C}_{18}\text{H}_{16}\text{O}_{10}$ , and the contact of which with a trace of ammonium-carbonate produces the violet before named (*ammonium-lokaëtin*).

Lokaëtin, when heated with dilute nitric acid at  $100^{\circ}$ , splits up into oxalic acid and a substance giving an intense yellow coloration with alkali. With concentrated sulphuric acid, lokaëtin is changed into a substance giving a deep blue with weak alkali. Its formula is  $\text{C}_{18}\text{H}_{12}\text{O}_8$ , i.e.,  $\text{C}_{18}\text{H}_{16}\text{O}_{10}$  minus  $2\text{H}_2\text{O}$ .

*Uses of Lokao, &c., in Dyeing.*—(1.) The liquor obtained by digesting crude lokao with water, and filtering, dyes cotton a pale green, but gives to wool and silk only a very pale bluish-grey, similar to the tint of some silks dyed by the Chinese. (2.) The deep violet ammonium-lokaëtin may be fixed upon cotton without a mordant, and also upon silk and wool. (3.) Ammonium-lokaëtin, added to a bath of sodium thiosulphate, gives a liquor which dyes cotton a very pure sky-blue, permanent in sunlight, and fast when washed.

B. J. G.

**New Synthesis of Diphenylketone.** By M. KOLLARITS and V. MERZ (Deut. Chem. Ges. Ber., v, 447—448).

DIPHENYLKETONE is formed, together with a small quantity of a substance having a very high boiling point, by heating a mixture of benzene and benzoic acid with phosphorus pentoxide to  $180^{\circ}$ — $200^{\circ}$ :—



By heating phosphorus pentoxide with benzoic acid alone, no ketone is formed, and benzene alone is not acted upon at all.

C. S.

**Synthesis of Mandelic Acid.** By O. MÜLLER (Deut. Chem. Ges. Ber., iv, 980).

THE compound of benzoic aldehyde and acid sodium sulphite is boiled for several hours with alcohol and potassium cyanide; potassium-sodium sulphite,  $\text{KNaSO}_3$ , then separates, and the clear alcoholic solution on evaporation leaves a thick brown fluid similar in appearance to "balsam of Peru." This is the impure nitrile of mandelic acid,  $\text{C}_6\text{H}_5\text{CH.OH.CN}$ . On boiling it with water and hydrochloric acid, evaporating to dryness, and then adding water and barium carbonate, a solution of barium mandelate is obtained. This, evaporated to dryness washed with a mixture of ether and alcohol until it becomes white, and then decomposed by dilute sulphuric acid, yields a solution from which the mandelic acid may be extracted by agitating it with ether. It only requires recrystallisation from water to be obtained in a state of purity.

C. E. G.

**Vanillic Acid.** By P. CARLES (Bull. Soc. Chim. de Paris, xvii, 13—16).

WHEN vanilla is kept for some time, it forms needle-shaped crystals, to which Stokkeby (*Zeitschr. f. Chem.*, 1865, 467) gave the name of vanillic acid. The discordant results obtained by him and by other investigators convinced the author that impure specimens had been employed. When purified by solution in water, decoloration with charcoal, and two or three recrystallisations, the acid appears in colourless transparent prisms, melting at  $80^\circ$ , very soluble in alcohol, ether, chloroform, bisulphide of carbon, fixed and volatile oils. One part dissolves in 83 of water at  $15^\circ$ ; it is readily soluble in boiling water. Its formula is  $\text{C}_8\text{H}_8\text{O}_3$ ; it is therefore isomeric with anisic, formobenzoic, methyl-salicylic, cresotic and oxytoluic acid.

The lead, magnesium, and zinc vanillates are the only stable salts obtained. With iodine two substitution-products,  $\text{C}_8\text{H}_7\text{IO}_3$  and  $\text{C}_8\text{H}_6\text{I}_2\text{O}_3$  are formed; with bromine only the primary  $\text{C}_8\text{H}_7\text{BrO}_3$ . By fusion with potash, oxyvanillic acid,  $\text{C}_8\text{H}_5\text{O}_4$ , is formed, which melts at  $169^\circ$ , and gives an intense green coloration with ferric salts, whereas vanillic acid gives a blue; its characteristics are otherwise very similar to those of that acid.

B. J. G.

**Isomerism in the Benzoic Series.** By F. BEILSTEIN and A. KÜHLBERG (*Ann. Chem. Pharm.*, clxiii, 121—143).

THIS paper is divided into the following sections:—

- I. Preparation of cinnamic acid (this Journal [2], x, 300).
- II. Nitro-cinnamic acids.



The para-acid has been already described (*loc. cit.*). By oxidation with chromic acid it yields para-nitro-benzoic acid.

The metanitrocinnamic acid is much more difficult to purify than the para-acid. It is separated from the latter by conversion into the ethyl ether. Ethyl meta-nitrocinnamate is very easily soluble in cold alcohol, whilst the corresponding para compound is almost insoluble. Meta-nitro-cinnamic acid is not very soluble in cold but easily soluble in boiling alcohol. It melts at 232°.

The barium salt forms pale yellow microscopic needles, containing 4H<sub>2</sub>O, which is almost wholly lost by exposure over sulphuric acid. The ethyl-ether by evaporation of its alcoholic solution appears as an oil which gradually crystallises. It melts at 42°.

III. Nitro-hydrocinnamic acid (see this Journal, *loc. cit.*).

IV. Meta-nitro-benzoic acid.

This compound, which until now has been missing, is obtained by the oxidation of meta-nitro-cinnamic acid. It is very readily separated from the isomeric para-nitro-benzoic acid in consequence of its much greater solubility in water; 100 parts of water at 16.5° dissolve .611 of the acid.

In cold alcohol or ether it is very easily soluble. It melts at 141°, or at almost exactly the same temperature as the ortho acid. But comparative experiments show that the meta acid is nearly three times more soluble in water than the ortho acid.

The barium salt [C<sub>7</sub>H<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub>]<sub>2</sub>Ba.3H<sub>2</sub>O differs from the barium salt of the ortho acid by its ready solubility in water.

Meta-nitro-benzoic acid reduced by tin and hydrochloric acid gives meta-amidobenzoic or anthranilic acid, of which the two sulphates containing H<sub>2</sub>O and 2H<sub>2</sub>O respectively, were analysed.

By the action of nitrous acid, the amido-acid was converted into salicylic acid, which was identified by its appearance, solubility, melting point and reaction with ferric chloride.

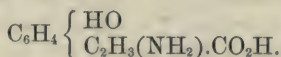
V. Nitro- $\alpha$ -toluic acid.

Radziszewski, by nitration of  $\alpha$ -toluic acid, obtained two nitro derivatives of which the one gave by oxidation para-nitrobenzoic acid, the other ortho-nitrobenzoic acid. The authors have repeated this experiment, but find that the supposed ortho acid is a mixture. Reduced by tin and hydrochloric acid and the resulting amido acid treated with nitrous acid, it furnished scarcely anything but salicylic acid; whence it is to be inferred that, by nitrating  $\alpha$ -toluic acid, a meta- in addition to a para-derivative is obtained.

VI. Indol. Baeyer and Emmerling succeeded in producing this body by fusion of nitro-cinnamic acid with caustic potash and iron filings. The authors, in repeating this experiment with pure para- and meta-nitro-cinnamic acids, have ascertained that it is the latter only which yields indol.

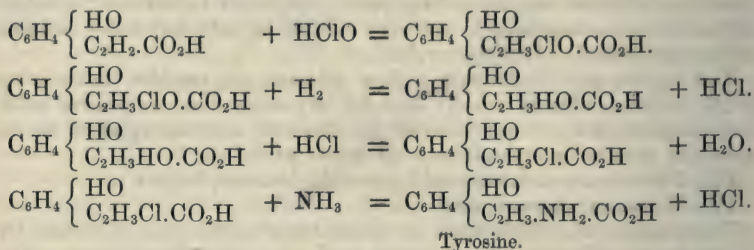
VII. Nitrophenyl-chloro-lactic acid (this Journal, *loc. cit.*)

VIII. Tyrosine. This body appears to have the constitution expressed by the formula—



In this case the synthesis of tyrosine would be realised by first converting para-nitro-cinnamic acid into para-oxycinnamic acid.

From this the hypochlorous acid compound, of which the corresponding nitro derivative has been described, might be produced, and the following series of reactions effected :—



W. A. T.

**Metanitrocinnamic Acid and Metanitrobenzoic Acid.** By F. BEILSTEIN and A. KÜHLBERG (Zeitschr. f. Chem., vii, 616—618).

CRUDE nitrocinnamic acid is a mixture of two isomerides, of which the para-acid is easily obtained in a pure state. To obtain the pure meta-acid, that portion of the crude acid which is most soluble in alcohol, is converted into the ethylic ether, and the latter is treated with small quantities of ether or alcohol, which dissolve the more soluble ether of the meta-acid. The crude ether obtained by evaporating these solutions is repeatedly treated in the same way until it is pure.

*Meta-nitro-cinnamic acid* is insoluble in water, sparingly soluble in cold, more freely in boiling alcohol. It melts at 232°, and sublimes with partial decomposition.  $[\text{C}_9\text{H}_5(\text{NO}_2)_2]_2\text{Ba} + 4\text{H}_2\text{O}$  crystallises in pale yellow microscopic needles, rather freely soluble in boiling water.  $[\text{C}_9\text{H}_5(\text{NO}_2)_2]_2\text{Ca} + 2\text{H}_2\text{O}$  forms pale yellow needles, and is more soluble than the barium-salt. The lead salt is but sparingly soluble in water and alcohol. The ethylic ether  $\text{C}_9\text{H}_5(\text{NO}_2)_2\text{O}.\text{C}_2\text{H}_5$  separates from a hot solution as an oil, which slowly crystallises; on spontaneous evaporation of the cold solution, it is obtained in long, thin needles, melting at 42° and readily dissolving in alcohol, ether, benzene or carbon disulphide. The *methylic ether* is readily soluble in boiling alcohol, sparingly in boiling water, and crystallises from the latter solution small needles melting at 72°—73°.

*Metanitrocinnamic acid* is readily oxidised by chromic acid to meta-nitrobenzoic acid; as the latter is much more soluble than the para-acid, the crude nitrocinnamic acid may be used for its preparation. *Metanitrobenzoic acid* crystallises from water in small needles, readily soluble in cold alcohol and ether. It melts at 141°, the same temperature at which orthonitrobenzoic acid melts, but it differs from the latter by being more soluble in water (100 parts of water dissolving at 16.5°, 0.61 parts of the meta-acid and only 0.235 of the ortho-acid); the

barium and zinc salt of the former are also more soluble than the salts of the ortho-acid.

$[C_7H_4(NO_2)_2]_2Ba + 3H_2O$  forms radiated crystalline groups.

$[C_7H_4(NO_2)_2]_2Ca + 2H_2O$  is very soluble in water and crystallises in small, thin needles.  $[C_7H_4(NO_2)_2]Pb + H_2O$  is sparingly soluble in cold water and crystallises in small brilliant prisms. The zinc salt is obtained as a syrup which gradually crystallises. The ethyl-ether melts at  $30^\circ$ , and the amide crystallises in short needles.

That this nitro-acid belongs to the meta-series was proved by converting it into anthranilic acid and salicylic acid.

Baeyer and Emmerling obtained *indol* by heating para-nitrocinnamic acid with potash and iron filings; but on repeating these experiments, the authors found that the pure para-acid does not yield a trace of indol, whilst the meta-acid is easily converted into this compound, which as is known, belongs to the meta-series.

Radziszewsky prepared from  $\alpha$ -toluic acid, two isomeric nitro-acids, one being the para-compound and the other, as he believed, the ortho-acid; but the latter is meta-nitro- $\alpha$ -toluic acid, as on oxidation it yields metanitrobenzoic acid, which was converted into anthranilic acid and salicylic acid.

The mononitro-products of toluene, cinnamic acid and  $\alpha$ -toluic acid show that when a para-compound is produced, a meta-compound is always formed at the same time.

C. S.

### On Amidodracrylic and Carboxamidodracrylic Acids. By PETER GRIESS (J. pr. Chem. [2], v, 369—371).

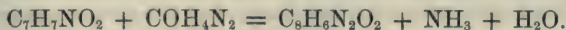
THESE two acids are obtained by fusing a mixture of urea and amidodracrylic acid.

*Uramidodracrylic acid*,  $C_7H_5\left(\begin{smallmatrix} CO \\ H_3 \end{smallmatrix}\right)N_2O_2$ , crystallises in anhydrous, white plates, difficultly soluble even in boiling water. It is obtained with these properties, however, only when very small quantities of material are operated upon; if more than 3 grams of the two substance be fused together, the product crystallises in minute, round forms which, when viewed under the microscope, are seen to bear a certain resemblance to yeast cells. All attempts to obtain these two modifications similarly crystallised have been unsuccessful; both, however, yield exactly the same products of decomposition. The latter modification is also obtained by the action of potassium cyanate on amidodracrylic hydrochloride.

*Carboxamidodracrylic acid*,  $C_7H_5H\left(\begin{smallmatrix} CO \\ CO \end{smallmatrix}\right)NO_2$ . This acid bears the greatest

resemblance to the isomeric carboxamidobenzoic acid. It crystallises in minute needles, which are insoluble in all neutral solvents.

On fusing anthranilic acid with urea, no uramido-acid is obtained, but the following decomposition occurs:—





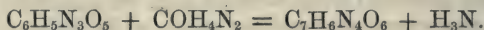
The compound  $C_8H_6N_2O_2$  is identical with the product of the action of hydrochloric acid on the ether produced by treating an alcoholic solution of anthranilic acid with cyanogen.

H. E. A.

### On Uramidodinitrophenylic Acid and some of its Derivatives.

By P. GRIESS (J. pr. Chem. [2], v, 1—6).

ON adding picramic acid to an equal quantity of fused urea, ammonia is evolved, and the whole soon solidifies to a brown mass. This is dissolved in dilute ammonia and hydrochloric acid added to the solution. The new acid is thereby precipitated and may be purified by repeated crystallisation from boiling water. Its formation is thus represented:—



*Uramidodinitrophenylic acid*,  $C_7H_6N_4O_6 = C_6H_3\left[\begin{smallmatrix} CO \\ H_3 \end{smallmatrix}\right]N_2\} (NO_2)_2O$ , is soluble with difficulty in boiling water and crystallises out on cooling in long, narrow plates of a bright yellow colour. It is readily soluble in hot alcohol, and yields crystalline salts with bases. Its barium salt forms blood-red needles, and its silver salt,  $C_7H_5N_4O_6Ag$ , is a reddish-yellow amorphous precipitate.

*Amido-uramidonitrophenylic acid*,  $C_7H_8N_4O_4 = C_6H_3(NH_2)\left[\begin{smallmatrix} CO \\ H_3 \end{smallmatrix}\right]N_2\} (NO_2)O$ , is prepared from the acid just described by treating it with ammonium sulphide. The blood-red solution is carefully decomposed by hydrochloric acid and the precipitate treated with hot water. After separation of the sulphur by filtration, the solution is first rendered alkaline by ammonia and then acidified with acetic acid. The acid thus obtained crystallises in reddish-brown needles, which are soluble with difficulty both in hot water and alcohol, and scarcely soluble in ether. It forms compounds both with acids and bases, the latter being very stable. The hydrochloric acid compound,  $C_7H_8N_4O_4.HCl$ , is precipitated in white, glistening scales on adding concentrated hydrochloric acid to a solution of the new acid in warm dilute hydrochloric acid. It is readily soluble in pure water. On mixing a hot concentrated ammoniacal solution of amido-uramidonitrophenylic acid with barium chloride, the barium compound  $(C_7H_7N_4O_4)_2Ba + 3\frac{1}{2}H_2O$ , is precipitated in steel-blue glistening needles, which are readily soluble in hot water and but slightly in the cold.

*Amido-carboxamidonitrophenylic acid*,  $C_7H_5N_5O_2 = C_6H_3(NH_2)[(CO)N](NO_2)O$ . On boiling the hydrochloric acid solution of amidouramidonitrophenylic acid for a quarter of an hour, ammonia is eliminated, and on cooling solidifies to a pulp of crystals, consisting of the new acid. This acid dissolves with difficulty in boiling water, and crystallises therefrom in golden-yellow needles. It is much more soluble in alcohol than in water, but only slightly soluble in ether. This acid, like the preceding one, combines both with acids and bases, but the former compounds are

very unstable. The hydrochloric acid compound,  $C_7H_5N_3O_4.HCl + H_2O$ , formed by dissolving the acid in hot, moderately concentrated hydrochloric acid, crystallises in white glistening plates, which at  $100^\circ$  lose both their water and hydrochloric acid, leaving pure amidocarboxamidonitrophenylic acid. The barium salt,  $(C_7H_4N_3O_4)_2Ba$ , forms yellow difficultly soluble needles.

*Diamidocarboxamidophenylic acid*,  $C_7H_7N_3O_2 = C_7H_3(NH_2)_2[(CO)N]O$ . Amidocarboxamidonitrophenylic acid, when treated with tin and hydrochloric acid, yields a very difficultly soluble tin double salt of the new acid. On decomposing this with sulphuretted hydrogen, the hydrochloric acid compound of the new acid,  $C_7H_7N_3O_2.HCl$ , is obtained in white plates, which become brown when exposed to the air in the moist state. The free acid, prepared from this by the addition of ammonia to its solution in boiling water, forms needles which are difficult to obtain colourless, as they oxidise and become brown on exposure to the air. This acid is but very slightly soluble in boiling water, and still less so in alcohol or ether. It combines with mineral acids, forming monacid compounds, and dissolves in potash-solution and in baryta-water, but is precipitated again by carbonic acid.

C. E. G.

**On Chrysanic Acid.** By H. SALKOWSKY (Ann. Chem. Pharm., clxiii, 1—64).

CHRYSANISIC acid was discovered by Cahours in 1845 (Ann. Chim. Phys. [3], xxvii, 454). He obtained it by treating nitranisic acid\* with fuming nitric acid and exhausting the product with ammonia in order to separate it from di- and trinitroanisol, which are also formed in large quantity at the same time. Cahours assigned to chrysanic acid the formula,  $C_7H_5N_3O_7$ , and regarded it as methylated picric acid; but Beilstein and Kellner found afterwards that the true formula of this acid is  $C_7H_5N_3O_6$  (Ann. Chem. Pharm., cxxviii, 164); their researches, however, do not give any clue as to the constitution of the chrysanic acid. The author undertook therefore a new investigation of this interesting body, and found that it is nothing but *dinitroamido-benzoic acid*,  $C_6H_2(NO_2)_2(NH_2)CO_2H$ , as the following reactions prove:—

(1.) By reduction with tin and hydrochloric acid it is converted into *triamidobenzoic acid*,  $C_6H_2(NH_2)_3CO_2H$ , which by the action of heat is resolved into carbon dioxide and *triamidobenzene*,  $C_6H_3(NH_2)_3$ .

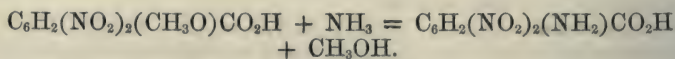
(2.) By heating chrysanic acid with fuming hydrochloric acid, it is converted into *trichlorobenzoic acid*,  $C_6H_2Cl_3.CO_2H$ .

(3.) By the action of nitrous acid, a *dinitrooxybenzoic acid*,  $C_6H_2(NO_2)_2(OH)CO_2H$ , is obtained; the same transformation is effected by the action of caustic alkalis.

\* In the translation of Cahours' paper in Liebig's *Annalen* it is said that Cahours used "anisic acid," and the same mistake occurs in Gmelin's *Handbook*. The author has convinced himself that only nitroanisic acid can be converted into chrysanic acid, and that anisic acid does not yield a trace.



The formation of chrysanisic acid shows that it cannot be a direct product of the action of nitric acid upon nitroanisic acid; it is formed only by the action of ammonia upon the crude product, which contains *dinitroanisic acid*, the latter being acted upon according to the following equation:—



Pure chrysanisic acid, prepared according to Cahours' method, melts at 259°, and not, as Cahours states, at a gentle heat. It crystallises from alcohol in small shining rhombic plates and from hot water in hair-like fasciculated needles. It is not quite insoluble in cold water, but insoluble in dilute acids.

By adding a small quantity of chrysanisic acid, or of one of its salts, to an alcoholic potash-solution, an almost black colour is produced, which disappears on standing and quickly on addition of water. This reaction may be used for the detection of this acid; the dark compound formed is perhaps  $\text{C}_6\text{H}_2(\text{NO}_2)_2\text{NHK.CO}_2\text{K}$ .

*Methyl chrysanisate* is obtained by heating the silver salt with methyl iodide; it crystallises from alcohol in small plates, melting at 144°, and having a metallic-golden lustre.

*Triamidobenzoic acid*,  $\text{C}_6\text{H}_2(\text{NH}_2)_3\text{CO}_2\text{H}$ , crystallises from a hot aqueous solution in fine shining needles, which in the pure state are almost colourless, but generally have a chocolate colour. It is sparingly soluble in cold water and nearly insoluble in alcohol and ether; the solution has an acid reaction. It combines not only with bases, but also with acids.

The *hydrochloride*,  $\text{C}_6\text{H}_2(\text{NH}_2)_3\text{CO}_2\text{H.2HCl}$ , is obtained by treating the liquid, after reduction, with hydrogen sulphide. It is very readily soluble in water and crystallises in silver-grey needles; the aqueous solution undergoes decomposition on exposure to the air, with separation of brown amorphous flakes. With platinic chloride it does not give a double salt, but a black residue; it combines however with stannous chloride; this compound, having the composition  $\text{C}_6\text{H}_2(\text{NH}_2)_3\text{CO}_2\text{H.2HCl.SnCl}_2 + 3\frac{1}{2}\text{H}_2\text{O}$ , is obtained on evaporating the product of reduction and forms monoclinic crystals. The *sulphate*,  $\text{C}_6\text{H}_2(\text{NH}_2)_3\text{CO}_2\text{H.H}_2\text{SO}_4 + \text{H}_2\text{O}$ , forms hard brownish crystals, sparingly soluble in boiling water. The *nitrate*,  $\text{C}_6\text{H}_2(\text{NH}_2)_3\text{CO}_2\text{H.2HNO}_3$ , crystallises in small rhombic six-sided brown plates, and is moderately soluble in cold water. The *oxalate* is obtained in fasciculated needles on mixing the hot concentrated solutions of the two acids.

The salts of the alkali-metals and magnesium could not be obtained in crystals. *Calcium triamidobenzoate*,  $[\text{C}_6\text{H}_2(\text{NH}_2)_3\text{CO}_2]_2\text{Ca}$ , is obtained by neutralising the acid with lime carbonate, and forms brown, hard crystalline crusts. *Zinc triamidobenzoate*,  $[\text{C}_6\text{H}_2(\text{NH}_2)_3\text{CO}_2]_2\text{Zn} + 6\text{H}_2\text{O}$ , forms hard, light-brown shining crystals.

The aqueous solution of triamidobenzoic acid does not dissolve lead oxide, but on evaporating it with lead acetate small shining prisms separate out, which, when once formed, are quite insoluble in water. The solution of the free acid is precipitated by copper, silver, and



mercuric salts; ferric chloride produces a violet-brown precipitate, the solution containing ferrous chloride.

*Triamidobenzene*,  $C_6H_3(NH_2)_3$ , is obtained by distilling a mixture of the acid with powdered glass. It is a crystalline solid, the colour of which varies between flesh-colour and chocolate. It is readily soluble in water, alcohol, and ether, and remains on evaporation as a radiate crystalline mass, melting at about  $103^\circ$  and distilling at  $336^\circ$  (corrected), and readily sublimes at a much lower temperature. The aqueous solution has a strong alkaline reaction, and gives with ferric chloride first a violet and then a brown precipitate, and with hypochlorites and nitrites brown precipitates. It reduces an ammoniacal silver-solution in the cold. On dissolving triamidobenzene in concentrated sulphuric acid and adding a trace of nitric acid, the liquid assumes first a dirty green colour, which soon changes into a fine blue and disappears on standing or by diluting with water. The same reaction is shown by triamido-benzoic acid.

Triamidobenzene combines with two equivalents of an acid forming very stable salts. *Triamidobenzene hydrochloride*,  $C_6H_3(NH_2)_3 \cdot 2HCl$ , crystallises in shining needles; it is very soluble in water, but only sparingly in concentrated hydrochloric acid. The *hydriodide* is also readily soluble and forms long radiate needles. *Triamidobenzene sulphate*,  $C_6H_3(NH_2)_3 \cdot H_2SO_4 + 2H_2O$ , crystallises in large plates.

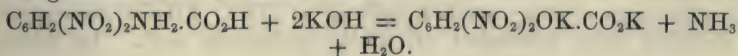
*Trichlorobenzoic acid*,  $C_6H_2Cl_3 \cdot CO_2H$ , is obtained by heating chrysanic acid with concentrated hydrochloric acid for 9 hours to  $200^\circ$ — $210^\circ$ . On opening the tubes, currents of nitrogen and carbon dioxide escape, and the residue contains ammonium chloride and some nitro-products. Pure trichlorobenzoic acid crystallises from dilute alcohol in pure white needles, melting at  $203^\circ$  but subliming at a lower temperature; it is almost insoluble in cold and sparingly soluble in hot water. *Silver trichlorobenzoate*,  $C_6H_2Cl_3 \cdot CO_2Ag$ , is a white precipitate, crystallising from boiling water in microscopic needles. *Calcium trichlorobenzoate*,  $(C_6H_2Cl_3 \cdot CO_2)_2Ca + 6H_2O$ , is but slightly soluble in cold water and crystallises from a hot solution in small shining needles. *Barium trichlorobenzoate*,  $(C_6H_2Cl_3 \cdot CO_2)_2Ba + 4H_2O$  crystallises from a hot solution in small prisms. The ethyl ether is insoluble in water and crystallises from alcohol in fine needles, melting at  $86^\circ$ .

*Trichlorobenzoyl chloride*,  $C_6H_2Cl_3 \cdot COCl$ , is obtained by the action of phosphorus pentachloride on the acid. It is readily soluble in ether, benzene, and carbon disulphide, and forms hard prisms, melting at  $36^\circ$ ; it has a faint but penetrating smell.

*Trichlorobenzamide*,  $C_6H_2Cl_3 \cdot CO \cdot NH_2$ , is produced by heating the chloride with ammonia. It is readily soluble in alcohol and ether and crystallises in very small needles, melting at  $176^\circ$ .

The reaction by which this trichlorobenzoic acid (which is isomeric with the known acid) is formed, is the first example of the replacement of amido- and nitro-groups by chlorine.

*Dinitro-oxybenzoic acid*,  $C_6H_2(NO_2)_2(OH) \cdot CO_2H$ , is produced by the action of nitrous acid on a boiling solution of chrysanic acid, and by boiling this acid with caustic alkalis—



It crystallises from hot water in large, thin rhombic plates, having a light-yellow or bronze colour and a very peculiar appearance, consisting of a number of smaller plates grown parallel one above another. From alcohol it crystallises in long octagon plates, grown together in cross-shape. It melts at about  $235^{\circ}$ — $237^{\circ}$ , and forms two series of explosive salts.

The *neutral potassium salt*,  $C_6H_2(NO_2)_2OK.CO_2K + 2H_2O$ , forms orange-red triclinic crystals with a greenish lustre, and is readily soluble in water. The *acid potassium salt*,  $C_6H_2(NO_2)_2OH.CO_2K$ , is much less soluble, and crystallises in small shining yellow plates.

The *neutral barium salt*,  $[C_6H_2(NO_2)_2O.CO_2]_2Ba + 7H_2O$ , crystallises in shining dark yellow needles. The *acid salt*,  $[C_6H_2(NO_2)_2OH.CO_2]_2Ba + 5H_2O$ , forms fine long yellow needles grouped in stars or in rhombic plates. The *neutral silver salt*,  $C_6H_2(NO_2)_2OAg.CO_2Ag$ , is obtained by boiling the aqueous solution of the acid with silver carbonate, and crystallises in brown needles. The *acid salt* obtained in a similar way forms shining orange needles.

The *acid ethyl-ether*,  $C_6H_2(NO_2)_2OH.CO_2(C_2H_5)$ , is produced by passing hydrochloric acid gas into an alcoholic solution of the acid. It is almost insoluble in cold water, and crystallises from hot water and alcohol in needles melting at  $87^{\circ}$ . It is a monobasic acid and decomposes carbonates. The *potassium-salt*,  $C_6H_2(NO_2)_2OK.CO_2(C_2H_5)$ , forms small yellow needles, and the *silver-salt* crystallises from hot water in yellowish red needles.

That this ether has really the constitution assigned to it is proved by the fact that it is not decomposed by boiling it with ammonia; but nitro compounds containing the group  $OC_2H_5$  in the aromatic nucleus under these circumstances, readily exchange this group for  $NH_2$ , whilst those containing the group  $CO_2C_2H_5$ , are either not acted upon at all, or exchange the alcohol-radical for  $NH_4$ .

The *diethyl ether*,  $C_6H_2(NO_2)_2O(C_2H_5)_2.CO_2(C_2H_5)$ , is most readily produced by heating the silver salt of the acid ether with ethyl iodide. It is readily soluble in alcohol, and crystallises in thin needles or small plates melting at  $59^{\circ}$ .

This acid is isomeric with dinitrosalicylic acid, and, apparently, not identical with Barth's dinitroparaoxybenzoic acid, although it has the groups  $HO$  and  $COOH$  in the same position as the latter.

Dinitroxybenzoic acid is easily reconverted into chrysanic acid by heating the diethyl-ether with aqueous ammonia to  $100^{\circ}$ . This reaction gave the clue to the mode of formation of the acid, which cannot be formed by the action of nitric acid on nitroanisic acid. That the product thus obtained does not contain any chrysanic acid, before treatment with ammonia, is proved by the fact that it is not coloured black by caustic potash-solution, but assumes a fine red colour, indicating the presence of the group  $OCH_3$  or  $OC_2H_5$ , and on heating no ammonia is evolved. It contains *dinitroanisic acid*,  $C_6H_2(NO_2)_2OCH_3.CO_2H$ , which can be isolated by treatment with a dilute solution of sodium carbonate and precipitation with hydrochloric acid. This acid crystallises from alcohol in thin, faint-yellow needles, and from hot water in large shining needles, melting at  $173^{\circ}$ . Alkalis decompose it at once, with formation of dinitrooxybenzoic acid. In dilute



ammonia it dissolves without decomposition, but on allowing the solution to stand, or by using stronger ammonia, it is converted into chrysanisic acid.

*Potassium dinitroanisate*,  $C_6H_2(NO_2)_2OCH_3.CO_2K + H_2O$ , is formed by saturating the acid with potassium bicarbonate. It is very soluble in water, and crystallises in yellow needles. The silver-salt is anhydrous, and crystallises from hot water in thick fascicles of nearly colourless needles; by heating it with ethyl iodide the ether is obtained, which crystallises from a hot alcoholic solution in shining monoclinic prisms.

By boiling chrysanisic acid with nitric acid, it is converted into picric acid, as Cahours has already found. Dilute sulphuric acid acts only at  $200^\circ$ , when the chrysanisic acid is completely destroyed, with formation of ammonium sulphate and carbonaceous matter. By the action of potassium cyanide it is converted into a compound belonging to the group of "isopurpuric acids;" the potassium salt is a brick-red powder.

Kellner and Beilstein describe an isomeride of chrysanisic acid, which is formed at the same time as the latter, but the author has found that this  $\beta$ -chrysanisic acid is identical with chrysanisic acid.

C. S.

### Two New Isomeric Sulpho-Acids of Amidobenzoic Acid. By PETER GRIESS (J. pr. Chem. [2], v, 244—247).

If a solution of amidobenzoic acid in fuming sulphuric acid be heated to about  $170^\circ$ , it soon solidifies to a dirty-white crystalline mass, which is a mixture of two isomeric acids of the formula  $C_7H_5(NH_2)O_2.SO_3$ ; these are readily separated by fractional crystallisation of the barium salts.

From the more soluble salt, which has the composition  $C_7H_5(NH_2)O_2.SO_3Ba + 3aq.$ , the free acid is obtained by decomposition with hydrochloric acid; it is anhydrous, and forms white, six-sided plates, very difficultly soluble in water, alcohol, and ether.

The second acid, obtained from the less soluble barium salt,  $C_7H_5(NH_2)O_2.SO_3Ba + 2aq.$ , crystallises with one molecule of water in long, narrow, four-sided plates, moderately soluble in hot water.

The same two acids are produced when cyanamidobenzoic acid (*Zeitschr. f. Chem.*, 1867, 534) is acted upon by fuming sulphuric acid.

Limpricht and Usler have prepared an amido-sulphobenzoic acid by reduction of nitrosulphobenzoic acid; probably this acid is isomeric with the above.

H. E. A.

### The Sulpho-Acids of Aniline Blue. By C. BULK (Deut. Chem. Ges. Ber., v, 417—422).

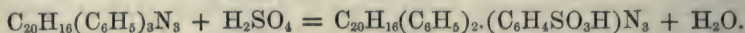
THE author has prepared four different sulpho-acids by the action of concentrated sulphuric acid upon aniline blue.

1. Triphenylrosaniline-monosulphonic acid.

By dissolving triphenylrosaniline hydrochloride in strong sulphuric



acid, heating the solution to 30° for 5—6 hours, and adding water, a dark blue bulky precipitate is obtained, which, when dried on the water-bath, appears as small grains with a metallic lustre—



This is the monosulphonic acid, which forms with alkalis salts easily soluble, with the earths and heavy metals salts difficultly soluble in water.

The sodium salt is known as "Nicholson's blue."

Solutions of the salts of this acid are all strongly coloured, the colour being increased by acidifying the solution, thus setting free the sulpho-acid.

By the action of reducing agents upon this acid, leucaniline is produced.

2. Triphenylrosanilinedisulphonic acid; and 3, trisulphonic acid.

These acids are simultaneously produced by heating a solution of triphenylrosaniline hydrochloride in six times its weight of strong sulphuric acid to 60° for 5 hours, and adding water, when there forms a blue flocculent precipitate, consisting chiefly of the *di*-sulpho-acid; from the filtrate hydrochloric acid or common salt precipitates the *tri*-sulpho-acid.

The di-acid forms easily soluble salts with alkalis; the sodium salt is known as "soluble blue." Its salts are more soluble than, and are thus distinguished from, those of the monosulphonic acid.

4. Triphenylrosaniline-tetrasulphonic acid.

Produced by digesting at 140° for several hours a solution of aniline blue in 10 times its weight of fuming sulphuric acid, adding water, precipitating excess of sulphuric acid by means of lead carbonate, filtering, evaporating the filtrate, and decomposing the lead salt thus formed.

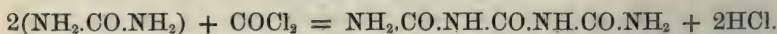
The acid is easily soluble in water; the solution evaporated on the water-bath yields an amorphous mass with metallic lustre; with metals it forms salts very soluble in water, generally insoluble in alcohol. By reducing the lead salt with ammonium sulphide, the corresponding leucaniline is produced.

The author has also prepared the sulpho-acids of aniline violet; these are in their chemical and physical properties exactly analogous to the acids already described, but are somewhat more difficult to prepare. A sulpho-acid of ethylphenylrosaniline has also been prepared, but as yet the author cannot definitely give its composition.

M. M. P. M.

### On the Action of Liquid Phosgene upon some Amides. By E. SCHMIDT (J. pr. Chem. [2], v, 35—66).

WHEN urea is heated with an excess of phosgene in sealed tubes for two days to 100°, the following reaction takes place:—



*Carbonyl urea*,  $\text{C}_3\text{H}_6\text{N}_4\text{O}_3$ , thus formed is a bulky white powder, consisting of microscopic needles, which are very sparingly soluble in cold

water, and more freely in boiling water; in cold alcohol it is almost insoluble. Heated on platinum foil it is resolved into ammonia and cyanic acid. On heating it slowly in a test-tube, it yields ammonia and cyanuric acid. It is soluble in concentrated acids, but does not combine with them. Neither does it form compounds with salts or bases, with the exception of mercuric oxide. The compound  $C_3H_6N_4O_3 + H_2O$  is obtained as a crystalline precipitate, which is insoluble in water, and decomposed by dilute acids.

Carbonyl-urea is further acted upon by phosgene when the two substances are heated up to  $150^\circ$ — $160^\circ$ , hydrochloric acid being formed, and a crystalline body, which was found to be a mixture of dicyanic and tricyanic (cyanuric) acids.

The dicyanic acid could not be obtained in a pure state.\*

By heating biuret and phosgene to  $60^\circ$  for 12 hours, *carbonyl-dibiuret*,  $C_5H_8N_6O_5$ , is formed.



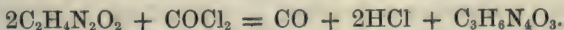
Carbonyl-dibiuret is a light, white crystalline powder, which is a little more soluble in water than carbonyl-urea, but almost insoluble in alcohol. It is soluble in alkalis and strong acids. When heated on platinum-foil it decomposes into carbon dioxide, ammonia, and cyanic acid, and when it is slowly heated in a small flask, ammonia and carbon dioxide are given off, and a residue containing urea, cyanuric acid, and ammelide is left behind.

On passing nitrous acid through a warm solution containing an excess of carbonyl-dibiuret, carbon dioxide is evolved, and as the liquid cools, urea nitrate crystallises out, mixed with a little cyanuric acid and ammonium nitrate. On boiling it with concentrated hydrochloric acid or potash-solution, it decomposes into ammonia, carbon dioxide, and cyanuric acid, whilst when boiled with baryta water, it yields carbon dioxide, cyanuric acid, and urea. Like carbonyl-urea it combines only with mercuric oxide; the compound  $C_5H_8N_6O_5 + 3HgO$  is a white bulky powder.

By the further action of phosgene upon carbonyl-dibiuret, it is resolved into two molecules of cyanuric acid:



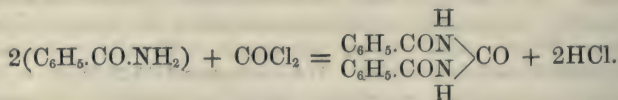
Phosgene and urea act on each other at  $100^\circ$ , no parabanic acid being, however, formed, as might have been expected, but carbonyl-urea—



Phosgene and benzamide heated together to  $160^\circ$ — $170^\circ$ , yield car-

\* By heating urea with cyanogen iodide, Poensgen (*Ann. Chem. Pharm.*, cxxviii, 345) obtained a compound called cyan-urea, which by the action of nitrous acid yielded dicyanic acid. Hallwachs doubts the existence of these compounds, and believes that the former compound is only impure ammelide, and the latter cyanuric acid. The author therefore repeated Poensgen's experiments, and found Hallwachs' supposition correct.

bon dioxide, benzoyl chloride, benzonitrile, and *carbonyl-dibenzamide*,  $C_{16}H_{12}N_2O_3$ , the latter compound formed according to the equation—



Carbonyl-dibenzamide is sparingly soluble in water, more freely in alcohol, and crystallises in fine silky needles. On boiling it with concentrated acids, it is decomposed into ammonia and benzoic acid, and when boiled for a long time with caustic potash-solution it yields carbon dioxide and benzamide.

*Carbonyl-diacetamide*,  $\begin{array}{c} CH_3.HCO \\ CH_3.HCO \end{array} \diagup \diagdown CO$ , is formed by heating acetamide and phosgene to  $50^\circ$ . It crystallises in rhombic needles; water and alcohol dissolve it but slowly in the cold, freely at a higher temperature. It melts when heated, and sublimes without decomposition.

By boiling it with concentrated acids, and with alkalis, it suffers similar decompositions as carbonyl-dibenzamide.

C. S.

### The Sulpho-urea corresponding to Pseudotoluidine. By

E. GIRARD (Deut. Chem. Ges. Ber., iv, 985).

WHEN pseudotoluidine is heated on the water-bath with carbon bisulphide in alcoholic solution as long as hydrogen sulphide continues to escape, sulphocarbopseudotoluidine separates out, partly during the reaction, but more abundantly on cooling. This compound, when recrystallised from alcohol, forms white, woolly needles, extremely soluble in alcohol and ether, melting at  $165^\circ$  (uncorr.), and giving by analysis numbers agreeing with the formula  $CS \left\{ \begin{array}{l} NH(C_7H_7) \\ NH(C_7H_7) \end{array} \right.$ .

H. W.

### Quinamine, a new Cinchona-alkaloid. By O. HESSE (Deut. Chem. Ges. Ber., v, 265).

THE new alkaloid has been discovered in the bark of *Cinchona succirubra*, now cultivated extensively in India. The process by which its isolation has been effected is not given, and the author has not yet analysed it. Quinamine is described as crystallising in delicate, asbestiform, anhydrous prisms. It is easily soluble in ether, alcohol, and petroleum spirit, slightly so in dilute alcohol, but is insoluble in water and in alkaline solutions. Its alcoholic solution is alkaline, and neutralises acids. The hydrochloride is amorphous; the neutral sulphate crystallises with difficulty in six-sided scales and short prisms.

The platinum-salt is a yellow, amorphous, very soluble precipitate, which can be obtained only from a concentrated aqueous solution of the hydrochloride. The gold-salt is a yellowish-white amorphous pre-



precipitate, which immediately becomes purplish-red from separation of gold.

Solutions of quinamine exhibit no fluorescence; neither do they give any green colour with chlorine and ammonia. The alkaloid melts at  $172^{\circ}$ , and crystallises again on cooling in radiated masses. Continued heating, however, renders it brown and amorphous.

W. A. T.

**Formation of Quinidine from Quinoidine.** By J. DE VRIJ  
(Chem. Centr., 1872, 152).

THIS method depends upon the difficult solubility of the double tartrate of quinidine. 100 grams of quinoidine are dissolved in 50 grams of tartaric acid, and 200 grams of water, and the solution is briskly agitated and set aside. In a few days a mass of crystals forms, which is pressed between folds of linen, dissolved in fourteen times its weight of water, and the solution filtered while hot. Double tartrate of quinidine crystallises out and is easily purified.

M. M. P. M.

**The so-called False Cinchona Barks.** By F. A. FLÜCKIGER  
(Chem. Centr., 1872, 152).

THE author refers to Hesse's alkaloid, *paytine*,  $C_{21}H_{24}N_2O + H_2O$ , obtained from *Quina blanca*. This bark the author has investigated, and says it is a new substance not hitherto seen in the market.

This alkaloid, differing from cinchonine only by the addition of one atom of carbon, and crystallising in a manner very like that in which cinchonine crystallises, is yet obtained from a so-called *false cinchona bark*.

This classification of false and true barks requires, in the author's opinion, to be altered.

M. M. P. M.

**Contributions to the knowledge of the Opium Bases.** By  
O. HESSE (Ann. Chem. Pharm., Suppl. Bd., viii, 261, Zeitschr. f. Chem. [2], vii, 641).

THE author has examined the mother-liquors obtained in the Robertson-Gregory method of morphine extraction (conversion into hydrochlorides by addition of calcium chloride to the opium extract, and crystallisation of the morphine, pseudomorphine, and codeine salts from the liquor). On addition of excess of ammonia to the mother-liquor diluted with its own bulk of hot water, an inconsiderable resinous precipitate of *lanthopine* is produced, the other bases remaining in solution. By agitation of the filtrate with ether, and of the ethereal extract with acetic acid, a mixture of acetates is obtained. Caustic soda added in excess precipitates *papaverine*, *narcotine*, *thebaine*, some *cryptopine*, and the three new bases, *protopine*, *laudanoline*, and *hydrocotarnine*, while the alkaline filtrate contains in solution *lanthopine*, *laudanine*, some *cryptopine*, *meconidine*? and *codamine*. These

last are again converted into acetates by the ether process, and the liquid is rendered neutral by ammonia. A little lanthopine separates after twenty-four hours, and the filtrate yields, with ammonia, a precipitate soluble in boiling dilute alcohol. On cooling, crystals of a mixture of laudanine and cryptopine separate. The alcoholic filtrate was found to contain no meconidine, although this base should be here obtained, whence the author concludes that the meconidine is decomposed by the Robertson-Gregory process, though not by the process adopted in his former researches. By evaporation of the alcoholic solution, and treatment with ether, a solution was formed, from which codamine was obtained, either by addition of fused calcium chloride, which causes water, colouring matters, and crystals of codamine to separate, or by conversion into acetate, thence into hydriodide, and purification of the latter.

The precipitate, insoluble in caustic soda, is digested with diluted alcohol, and acetic acid added till litmus-paper is faintly reddened by it. Addition of three times the volume of boiling water produces a crystalline precipitate of papaverine and narcotine (these bases not neutralising acetic acid). The filtrate from this, freed from alcohol by evaporation, gives, on addition of strong hydrochloric acid, a precipitate of cryptopine hydrochloride, but this method is not to be recommended, as the acid converts some of the thebaine into thebaicine (a non-crystalline isomeride), which interferes with the separation of the other bases. A better plan is to add tartaric acid, which causes a copious crystallisation of thebaine bitartrate. The mother-liquor of this is neutralised by ammonia, and mixed with 3 per cent. of its weight of sodium bicarbonate, made into a paste with water. After about eight days, a black pitchy mass has separated. The filtrate from this gives with ammonia a precipitate which is treated with boiling benzene, the filtrate being also extracted with benzene. Cryptopine and protopine are undissolved; while on shaking the benzene solution with a saturated aqueous solution of sodium bicarbonate, laudanosine crystallises out; and the benzene filtrate from this, treated with gaseous hydrogen chloride, yields hydrochloride of hydrocotarnine.

The author describes narceine as existing in the mother-liquors of the Robertson-Gregory process, but does not state how, or at what stage, it is separated from the other bases.

Sulphuric acid containing traces of ferric oxide gave, with several of these bases, colour reactions different from those given by pure acid. Pure sulphuric acid kept in glass bottles corrodes the glass, and takes up sufficient iron after a time to give entirely different reactions.

*Pseudomorphine*,  $C_{17}H_{19}NO_4$ , is only to be found occasionally in opium, being observed only once in good Smyrna opium during four years. It gives crystals with  $H_2O$ , and  $4H_2O$ . It forms a nitro-substitution product, which rapidly disappears in nitric acid. Reducing agents (sulphurous acid, sulphuretted hydrogen, nascent hydrogen) have no action on it.

*Lanthopine*, like pseudomorphine, narcotine, and papaverine, does not neutralise acetic acid. It gives no colour with ferric chloride.

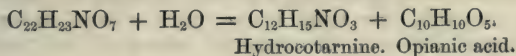
*Laudanine*,  $C_{20}H_{25}NO_4$ , and *cryptopine* are separated by dilute caustic soda, which dissolves the latter only sparingly. The filtrate is treated



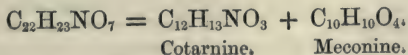
with sal-ammoniac, the precipitate thereby formed dissolved in acetic acid, and potassium iodide added, whereby a hydriodide of laudanine, free from cryptopine, is obtained. Concentrated caustic potash solution gives a crystalline compound with laudanine. The author found  $C_{20}H_{25}NO_3$  formerly as the formula of laudanine, but now adopts  $C_{20}H_{25}NO_4$ . For cryptopine he gives the formula  $C_{21}H_{23}NO_5$ . The body analysed by T. and H. Smith, and to which they attributed the formula  $C_{23}H_{25}NO_5$ , was contaminated with thebaine. The observation of these chemists, that the base forms two hydrochlorides, the one containing  $C_{23}H_{25}NO_5 \cdot HCl \cdot 5H_2O$ , the other,  $C_{23}H_{25}NO_5 \cdot 2HCl \cdot 6H_2O$ , is erroneous, only one,  $C_{21}H_{23}NO_5 \cdot HCl \cdot 6H_2O$ , being produced. Nitric acid of sp. gr. 1.06 forms nitro-cryptopine, which forms well characterised salts, the base being anhydrous, crystalline, and melting at  $185^\circ$ . Its formula is  $C_{21}H_{22}(NO_2)NO_5$ , which is the same as that of crystallised nitropapaverine, with which it is not identical, the latter containing water of crystallisation  $= C_{21}H_{20}(NO_2)NO_4 \cdot H_2O$ .

*Codamine*,  $C_{20}H_{25}NO_4$ , melts at  $126^\circ$  when crystallised from benzene, and at  $120^\circ$  when from alcohol or ether; ferric chloride gives a fine dark-green colour with separation of ferric oxide; it appears to form compounds with caustic alkalis: the author adopts the formula  $C_{20}H_{25}NO_4$  instead of the earlier one,  $C_{20}H_{23}NO_4$ .

*Narcotine*  $C_{22}H_{23}NO_7$ . The author corroborates the formula ascribed to this base by Matthiessen and Foster, in place of the older one,  $C_{23}H_{25}NO_7$ ; the base is separated from papaverine by solution in boiling water along with one-third part of oxalic acid; on cooling, the acid papaverine oxalate crystallises out; this process is repeated several times, and, finally, the narcotine is precipitated by ammonia and crystallised from boiling alcohol. It melts at  $176^\circ$ , and decomposes at a few degrees higher. On boiling with baryta-water, narcotine forms a base much resembling hydrocotarnine, readily soluble in ether, which the author considers to be formed by the reaction—



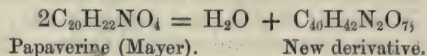
without, however, giving any analytical data: he infers that the action of water on narcotine is the same, and not that stated to take place by Matthiessen and Wright\* (*Proc. Roy. Soc.*, xvii, 340; also *Jahresbericht*, 1869, 729) (erroneously attributed to Matthiessen and Foster in the paper), viz.:—



\* *Note by Abstractor*.—It has been pointed out by the abstractor (*Proc. Roy. Soc.*, xx, 278) that there is reason for believing that narcotine and cotarnine are capable of forming a series of polymerides, and that the different properties of the so-called cotarnine, obtained in various ways, are probably due to the presence of these different polymerides. It is not impossible that the reaction with baryta-water may occur as Hesse explains it; but pure meconine is obtainable from narcotine by heating with water in sealed tubes (Matthiessen and Wright, *loc. cit. supra*), and a minute quantity of meconine is also formed when narcotine is decomposed by heating above its melting-point. The mutual relations of narcotine, cotarnine, and



*Papaverine*,  $C_{21}H_{21}NO_4$ . The author has formerly shown that the pure base has this formula, and not the one formerly attributed to it, viz.,  $C_{20}H_{21}NO_4$ , and considers that the supposed new derivative by the action of zinc chloride obtained by E. L. Mayer (*Deut. Chem. Ges. Ber.*, iv, 128) (considered by the latter to be formed by the reaction—



is only pure papaverine: Mayer's numbers agreeing well with those required for the formula  $C_{21}H_{21}NO_4 \cdot HCl$ .

By the action of nitric acid of sp. gr. 1.06, nitropapaverine is obtained =  $C_{21}H_{20}(NO_2)NO_4 + H_2O$ : when crystallised, in the dark it is colourless, but becomes yellow in the light; the water of crystallisation is only lost at  $163^\circ$ , when the substance melts and becomes coloured.

*Protopine*,  $C_{20}H_{19}NO_5$ , is separated from cryptopine by precipitation of the solution of the mixed hydrochlorides with strong hydrochloric acid; the protopine salt is horny, and adheres to the sides of the vessel, and is easily freed from the cryptopine salt by a little washing with water: a quantity of material that gave 80 grams of cryptopine, gave only about  $1\frac{1}{2}$  of protopine. It gives no colour with ferric chloride.

*Laudanosine*,  $C_{21}H_{27}NO_4$ , crystallises from alcohol, hot benzene, or ether; it melts at  $89^\circ$ , and gives no colour with ferric chloride.

*Hydrocotarnine*,  $C_{12}H_{15}NO_3 + \frac{1}{2}H_2O$ , dissolves readily, and without coloration, in alcohol, acetone, chloroform, benzene, and ether, and crystallises readily from the latter. The crystals melt at  $50^\circ$ , losing all their water of crystallisation at  $57^\circ$ . At  $100^\circ$  a great loss of weight is perceptible, without any appreciable alteration in composition; it cannot, however, be distilled under the ordinary pressure.

Pure sulphuric acid gives, on warming, distinctive colorations with the opium alkaloids, the tints being much altered in many cases by traces of impurity of iron or oxides of nitrogen: the author divides them into groups by this means:—

I. $\alpha$ . Morphine, pseudomorphine, codeine.	Dirty dark-green (morphine group).
$\beta$ . Laudanin, codamine, laudanosine.	Dirty red-violet (laudanin group).
II. Thebaine, cryptopine, protopine.	Dirty green to brown-green (thebaine group).
III. $\alpha$ . Papaverine.	Dark violet (papaverine group).
$\beta$ . Narcine, lanthopine.	Black-brown to dark-brown (narcine group).
IV. Narcotine, hydrocotarnine.	Dirty red-violet (different shade from that of I. $\beta$ ) (narcotine group).

Group I  $\beta$  give a dark-violet tint with acid containing iron, while IV give still a dirty-red violet, as with the pure acid.

C. R. A. W.

hydrocotarnine require further investigation; not improbably the last is not a normal constituent of opium, but is formed, like meconine, by the decomposition of other substances, *e.g.*, narcotine, during the process of extraction.—C. R. A. W.

## XXIX.—ON DEACON'S METHOD OF OBTAINING CHLORINE, AS ILLUSTRATING SOME PRINCIPLES OF CHEMICAL DYNAMICS.

(*A Lecture delivered to the Fellows of the Chemical Society, June 20, 1872.*)

By HENRY DEACON, Alkali Manufacturer, Widnes.

### *Nature of the Enquiry.*

My problem has been how, readily, regularly, and continuously to make from a heated current of hydrochloric acid gas, mixed with air, the largest quantity of chlorine in the smallest space, in the shortest time, at the least cost.

The research has gradually resolved itself into the following enquiries:—

1. As to the most suitable active or catalytic substance.
2. Whether the mass or the surface of the substance was the active element.
3. As to the effect of various temperatures.
4. As to the best arrangement of the substance.
5. As to the effects produced in and by currents of gas of different velocities; *i.e.* the effect of longer or shorter time of contact of the gas and active substance.
6. As to the effect of various proportions of air or of oxygen and hydrochloric acid.

### *1. As to the Active or Catalytic substance employed.*

Within the range of temperature I have employed, hydrochloric acid is not decomposed by air or oxygen when in or passing through hard glass combustion-tubes; the rule observed being that when the solid is not acted upon by hydrochloric acid, no chlorine is produced, but in all cases where a chloride is formed that is decomposable with the evolution of chlorine by heated dry air, hydrochloric is decomposed. The amount of action on the substance, however, bears no ascertainable proportion to the amount of chlorine obtained: usually by comparison, it is indefinitely

small. Amongst this class of substances may be named the clays, most pumice stones, oxide of iron, and oxide of chromium. I have experimented with iron and chromium in many ways, but always with the same result of exceedingly feeble action. To the extent that chromic acid or perchloride of iron can be formed chlorine can be obtained by an intermittent action, but not in any material degree by a continuous action.

To obtain the reaction in the highest degree the affinity for both chlorine and oxygen must co-exist. The element must be *able* to form not only a chloride which in dry hot air is decomposed, but it must also be *able* to form at the temperature worked with, an oxide or compound with oxygen. Copper has proved the most convenient element, and all the compounds of it which have been tried are eminently active. Not all in the same degree, but I have no measure of the difference between any, except between its chloride and sulphate, to which I shall again allude in speaking of the effects of temperature. Amongst the compounds of copper tried are its oxide, carbonate, acetate, borate, phosphate, silicate, arseniate, chromate, sulphate, and chloride; and all the different series of experiments to which I shall allude to-night, have been performed, with its sulphate, or with fragments of burnt clay, or of pumice stone saturated with it, with one exception when fragments of clay were saturated with cupric chloride.

Having for the sake of economy decided upon sulphate of copper, the next point was to ascertain to what extent it is changed by the reaction. On all occasions when chlorine is produced there are indications of cupric chloride. The quantity of cupric chloride however bears no ascertainable proportion to the weight of chlorine produced. It is often present in the merest traces. Pure sulphate of copper has been subjected to the action of hot hydrochloric acid and air for three or four weeks continuously, and gave only traces of cupric chloride at the end of the time. If, however, the heat be too high, the sulphate is very readily converted into chloride. So, too, if some base in the clay decomposes the sulphate, the chloride is usually formed with increased ease. Whilst the current of gas is passing and decomposition is proceeding, cupric chloride is not volatilised unless the temperature is too high, and at the temperature at which it is volatilised the decomposition of hydrochloric acid is reduced. In a tube where no current exists, and decomposi-



tion has ceased, (and notably in a sealed tube with the gases under pressure—some of the sulphate is more readily decomposed, and the chloride is volatilised. The conditions favourable to the decomposition of hydrochloric acid, fortunately for me, are unfavourable to the formation of cupric chloride in any material quantity. Still as it is always seen when chlorine is produced, the two phenomena appear to have an intimate relationship. But cupric chloride is not a pleasant substance for experiments. It is very apt to give extremely discordant results, being probably too unstable under the circumstances of these experiments to be sufficiently unaffected by slight changes.

*Method of Experimentation.*

In the following experiments, in some few cases, straight tobacco pipe stems, or tubes glazed externally with a lead glaze, were saturated internally with sulphate of copper solution, and were passed through one cork of a combustion tube. In one set of experiments two such tubes of the same length, but different bores, were placed side by side in a glass tube sealed at one end. The mixture of gases was introduced into the glass tube through the cork, through which the tobacco pipes also passed. The gases were drawn through the tobacco pipes alternately. The gases therefore traversed the glass tube before entering the tobacco pipes, and as first one of the pipes and then the other was used, the gas entered each at identically the same temperature. In each experiment the gases and active material were, as far as possible, heated to the same degree before coming into contact. Whether this was as successfully accomplished as was desired, is not free from doubt, especially in the cases where high velocities have been used. Still it is not thought that any large errors arise from this cause although they will all be in one direction. All the earlier experiments were performed by means of the ordinary laboratory gas combustion furnaces. Usually two were arranged end to end, the combustion tube going through both; it was empty in one, and contained the copper salt on bricks in the other; the gases passed first through the empty portion to be heated. The coal gas burnt was measured, and its rate of flow was watched by means of an anemometer, and regulated by hand to burn at a constant rate. No means at that time were available for ascertaining the temperature, so resort was had to a regulation of the quantity of fuel burnt. The gas was supplied by a small gas-works using a mixture of coals, and the gas varied sensibly in its heating powers at various times.

The mixed gases throughout all the experiments were contained in bell-glass gasholders worked with strong vitriol, and were therefore dry. In the earlier experiments the gases were aspirated by means of a Bunsen's pump, and measured by the readings of the bell-glass gasometer, and the flow regulated by the aid of an anemometer. In the earlier experiments also two gasometers were used, one for hydrochloric-acid, the other for air or oxygen; but this practice was discontinued in favour of mixing the gases together in one gasometer. The hydrochloric acid passed and chlorine obtained were in each case ascertained by analysis of the solution of pure caustic soda in which the absorption took place. This solution was kept cool to diminish the amount of chlorate formed. When analysed it was boiled with a protosalt of iron to decompose the chlorate present. The free chlorine was estimated by its oxidising effects, and the total chlorine by titration with a silver solution. In the later experiments, instead of a Bunsen's pump, a closed glass aspirator was employed, and the bulk of gases drawn was ascertained, with due precautions as to pressure and temperature, by the bulk of water run from the closed aspirator, the hydrochloric acid and chlorine being ascertained by analysis as before, and the readings of both gasometers being used to check each other. This second method is easier to work, and is better for ascertaining the constitution of the mixture of gases, which usually varies a little during each experiment, but does not give velocities so nearly equal as the former mode.

The furnace used with the second method was 6 ft. by 4 ft. in plan, 7 ft. high, made of bricks, and heated with coke. It contained a cast iron tube, 4 ft. 6 in. long, 3 in. thick, and 6 in. bore, weighing 13 cwt.; it was stopped at the ends by thick stones, the glass combustion tubes passing through. This massiveness was employed for the sake of securing uniformity of temperature. In this cast iron tube was inserted a pyrometer consisting of one brass and two iron rods, the different expansion of the rods being communicated by a train of levers and wheels to an index. The indications of this pyrometer were checked by means of a copper bolt, which being heated in the same place was quenched in water, and the temperature was calculated from the known weights and specific heats and rise of temperature of the water, and of the vessel containing it.

A fine platinum wire was subsequently also passed through the iron

tube, and its increased electrical resistance was measured by one of "Siemens'" universal galvanometers. In one series of experiments my assistant, Mr Rocholl, succeeded in drawing a fine glass tube, and through it threaded the wire, passed both safely through the glass combustion tube, and packed the active material safely round it; but this feat could not be repeated. It sufficed, however, to show there was no difference which this instrument would detect, between the temperature inside and outside the glass combustion tube during the experiment. All the other precautions were of the ordinary kind, and need no particular description.

*Limits of Experimental Errors.*

*Table A.*

When the time of an experiment was divided into two nearly equal portions, and the results of each half compared together, we obtained accordant results. But if the furnaces had cooled in the interval between two experiments, the slight changes in the position of the tube, &c., and other changes not so evident, always prevented our being able to ensure a repetition of results. Hence arose the practice, continued throughout, of rejecting all single experiments, and using only a series of two or more made in immediate succession, and under circumstances which excluded as far as possible the probability of any changes occurring in any of the circumstances.

In Table A are recorded the results of the experiments by which I ascertained the limit of errors to which this method of performing these experiments is liable. This Table gives the weights of the hydrochloric acid passed and chlorine obtained in grains, the duration of each portion of the experiment in minutes, and the percentage of hydrochloric acid decomposed. The hydrochloric acid and air were contained in separate gasholders, and the quantities passed were as nearly 4 HCl to 5 air as possible, a little under equivalent volumes, but the proportions were not analysed. It was intended to pass an equal volume of hydrochloric acid in the same time in each portion of an experiment; a comparison of the numbers in the two first columns will shew how far this succeeded. It is reasonable, I think, to assume that the variations of the air were no greater than those of the hydrochloric acid as indicated by the difference between its "twin" weights, and therefore I have assumed this table fairly to



afford data for a judgment as to the probable accuracy of the other results to which I am about to refer. Amongst this series of moderate errors, is one very large error occurring in the seventh "twin". There is a considerable divergence in the times, which should have been equal, and a much wider divergence in the results. The cause is unknown. In compiling the rest of the tables, I have omitted no experiments which vary in moderate degree, although the direction of the variation may be inverse to the average course. Such errors, if they are errors, are I think equally likely to be either above of below the truth, and should therefore be counted in an average. Of course all experiments known or believed to be defective in any condition are rejected, but records of all are preserved, for time may yet throw light on some of the variations at present inexplicable. No appreciable error is caused by any re-formation of hydrochloric acid. It is found by experiment that both prolonged and quick withdrawal of the gases from the hot combustion-tube, after they have passed the active substance, give the same results.

#### *Explanation of Tables I to XI.*

For convenience of argument and reference, all the rest of the experimental results are expressed in the same form. The proportion of O to 4 HCl is in volumes. The quantity of mixed gases are reckoned as fluid grains per minute for the comparison of velocities. The quantity of chlorine obtained per minute is in fluid grains. The percentage of hydrochloric acid decomposed is calculated. The pyrometric indications are given when observed, and the readings of the galvanometer when employed. The latter cannot be compared together, except in the same series of experiments, as the wire was sometimes changed between different series. The galvanometer readings therefore, as tabulated, only serve to show the direction and proportional extent of the variations in temperature in each series. The fluid grains are the bulk of a grain of water at 41°F. The gases are estimated as at a temperature of 32°F. and barometric pressure of 29.92 in. This bulk bears the same proportion to the grain-weight, that the cubic centimeter does to the gram, and may therefore be read as cubic centimeters for all calculations of proportion. For absolute comparison as to quantities, a cubic centimeter is equal to 15.4 fluid grains nearly. The order in which the experiments are arranged is not the order in which they were per-

formed. I have classified and arranged them to suit the argument I wish to develop.

2 & 3. *As regards Temperature and Mass.*

*Reference to Table 1, and Diagram 1.*

Turning now to the tables themselves: No. 1 contains the results of the chief experiments as to the effects of temperature. In Diagram 1 these results are shown graphically, the horizontal divisions representing degrees Fahrenheit, and the vertical divisions the percentage of hydrochloric acid decomposed. The percentage results should properly be corrected; but as these corrections would not materially affect the general tendency of the results obtained, and would have to be made on principles I have yet to explain, they are for the present omitted. Two separate sets of experiments were performed with pieces of fire-brick saturated with cupric sulphate, and one experiment with pieces of pure cupric sulphate as nearly as possible of the same size as the fire-bricks. Another experiment was performed with pieces of common bricks saturated with cupric chloride. The results show at first a gradual and then rapid increase of action with increased temperature up to a certain point, and then a diminished action with further increase of temperature. Pure cupric sulphate, *i.e.* in mass, and the same salt on brick, *i.e.* as surface, give the same results. *Surface, not mass, is therefore the measure of its action.* The lines connecting the results with cupric chloride are in advance of and parallel to those with the sulphate. The chloride is therefore proved to differ in action from the sulphate. I have before stated that with cupric sulphate there are always indications more or less feeble of the chloride, and that these indications increase with elevation of temperature. If the reaction is dependent on the presence of cupric chloride, the lines should converge as the quantity of chloride in the sulphate is increased by temperature. These experiments show no such convergence, nor did the contents of any of the tubes when examined at the end of the experiments show any loss of sulphuric acid. The pure cupric sulphate gave only faint opalescence when silver nitrate was added to its solution. The bricks impregnated with cupric sulphate gave a material quantity of aluminium chloride and small quantities of ferric chloride, but showed no loss of sulphuric acid, although part of the cupric sulphate was evidently decomposed by the clay, as it was no longer wholly soluble

in water. This has however been abundantly proved, by other experiments not now necessary to dwell upon, to be the action of the clay itself, and not any result of the chlorine reaction. Indeed the experiment with pure cupric sulphate is conclusive as to this point. A similar partial decomposition of the cupric chloride by the clay was also noticed, and, as was to be anticipated, the decomposition of the copper salt is very different with different clays and absorbent materials. The near approach to the vertical which the line of percentage decomposition assumes in one part of its course, points to the wide variation of results ensuing from small variations of temperature within the critical limits. Where the line begins to recurve, indications of cupric chloride were always increased, so that it may be said, when working with the sulphate, the more cupric chloride the less chlorine. The value of these comparisons between the action of cupric chloride, and of the pure sulphate is increased by the fact that three pairs of the experiments were performed simultaneously with identity of proportions of hydrochloric acid and oxygen and of temperatures. The pairs are 99a and 99b, 100a and 100b, and 101a and 101b.

At the horizontal line two sets of figures are given for temperatures. The upper line of the two gives the indications of the pyrometer; the lower line is calculated from the galvanometer readings, on the assumption that electrical resistance increases in simple proportion to increase of temperature. Each line is open to the objection that the specific heat of copper and electrical resistance do not vary in proportion to variation of temperature. I am unable to give the proper correction to meet these objections, so leave the record untouched. Another very remarkable point as to temperature occurs with experiments on the large scale. There the observed temperature is invariably lower than in these small-scale laboratory experiments; usually  $100^{\circ}$  to  $150^{\circ}$  lower. The cause is unknown. It arises, I think, in part from the fact that the reaction evolves heat, which in the small scale is quickly dissipated, but in the large scale is retained in the mass, many feet thick, and gradually accumulating would rise to a point at which cupric sulphate would be volatilised. We therefore on the large scale practically work with very extended surfaces at a low temperature, whilst in the laboratory we employ a concentrated surface at a high temperature, but I am not satisfied that this or any other at present known cause will adequately account for



all the difference. The experiments in Table 1 therefore must not be considered as doing anything beyond giving the points of temperature as ascertained by the method I have described, at which cupric sulphate &c. under all the conditions recited, will give the results recorded. Under other conditions the same temperatures will give other results. There is, however, no reason for believing that the results cannot always be compared amongst themselves. So far as I am able to judge, the curves indicated in diagram 1 would be repeated with all apparatus, although possibly at somewhat different temperatures. Another, and so to say common place inference from table 1 is, that a molecule of copper salt is more active, *i.e.* will do more work in a unit of time, within a limited range of high than of low temperatures.

4 & 5. *Best arrangement of substance, and action of velocity, or time of contact.*

*Reference to Tables 2, 3, 4, 5, 6, & 7, and to Diagrams 2, 3, 4, 5.*

The next portion of my experiments shows that the work done by, or with the aid of, a molecule of copper salt in a unit of time, is varied by mechanical forces or conditions, and I put my first proposition in the following words. *The work done in a unit of time by a unit of surface of a copper salt, that is to say by an active molecule of a copper salt, in streams of gas of different velocities, but of the same temperature, and of the same mixtures of hydrochloric acid and air, or of hydrochloric acid and oxygen, will depend upon its position with relation to the direction of the stream of gas.*

*If the active molecules form the surfaces of an irregular porous mass with which a tube is filled, then, as the velocities of the streams passing through the interstices increase, the work done by each molecule, as measured by the quantity or weight of hydrochloric acid decomposed in a unit of time, will also increase in nearly direct proportion.*

Table No. 2 gives the results with velocities varying from 1 to 2.70 (averaging from 1 to 1.96), whilst the weights of chlorine obtained vary from 282.1 to 501.6, or at the rate of 1 to 1.78, and the percentage of hydrochloric acid decomposed decreases from 48.34 per cent. to 43.74 per cent. or at the rate of 1. to .9.

Table No. 3 gives the results with much greater variations of speed, and the results of the two experiments with widest ranges of speeds,

are shown in diagrams on Velocities, 2 and 3. Comparing the results obtained with various temperatures, say No. 117 with Nos. 118, 131, and 111, there are indications that at the higher temperatures (and also with a larger proportion of oxygen) the weight of chlorine increases more rapidly with increase of velocities than at lower temperatures.

*If the active molecules line the bore of a long parallel tube, say the bore of a tobacco-pipe stem, then, as the velocities of the streams of gas increase within moderate limits, the work done by a molecule, as measured by the quantity or weight of hydrochloric acid decomposed in a unit of time will be nearly constant.*

Table No. 4, shows that with velocities increasing at the average rate of from 1 to 2.29, the weight of chlorine obtained, or of hydrochloric acid decomposed, increases only from 1 to 1.33, or allowing for corrections hereafter to be explained, the percentage decreases from 20.9 to 11.8 per cent., or at the rate of 1 to .56. Taking the results shown in Table 2, and applying them proportionately to the experiments shown in Table 4, an increase of velocity of from 1 to 2.29 should have given an increased weight of hydrochloric acid decomposed of from 1 to 1.98, and a decreased percentage decomposition of from 1 to .77. With the tubes described, the increased weight of hydrochloric acid decomposed in a unit of time at higher velocities is therefore only one-third of the increase obtained from the same surface, differently arranged with relation to the current of gas.

On comparing two similar tubes of the same kind, say tobacco-pipe stems of the same lengths, but with bores of different diameters, the foregoing results are again modified. Table 5 gives the results with two such tubes arranged in a glass combustion-tube sealed at one end as before described. Here with velocities varying from 1. to 2.45, we have quantities decreasing from 1.53 to 1., and (corrected) percentage decomposition decreasing from 1.527 to 1. But the increased velocity is in the small tube, that is in connection with the smaller surface or fewer active molecules; and this surface or number of molecules, being in proportion to the tubes' diameter is reduced from 1.54 in the larger tube and smaller velocity, to 1 in the smaller tube and higher velocity: reduced, that is to say, in the same proportion that the weight of

hydrochloric acid decomposed, and its percentage decomposition are reduced. In other words, in the case given, *the same number of active molecules of copper salt decomposes the same weight of hydrochloric acid in the same time in currents of different velocities in tubes of different diameters, where the difference of velocity is in inverse proportion to the sectional area of the bores of the tubes, i.e., in inverse proportion to the square of their diameters.*

*Theoretical explanations of different action of surface of long parallel tubes.*

In reflecting as to the cause of these differences in the action of a molecule of copper salt, the first conclusion appears to be that the cause is mechanical. Secondly, from the premises given, viz., the rough bore of a tobacco-pipestem, and a number of small fragments enclosed in a glass tube, it is evident the results must have much in common. For if a perfectly smooth tube will give results differing in kind from a perfectly irregular porous mass, then as the smooth tube becomes rough, and the irregular mass becomes regular (as for example, where it touches the glass tube), the phenomena proper to each distinct construction must overlap, and the rough tube will give results approximating to the mass, and the mass will give results approximating to the tube.

A possible source of error arises in all these experiments, (excepting always those with the two tobacco-pipes in the sealed glass tubes,) tending to lower the result of higher velocities, viz., that the time for the gases to become heated before contact with the copper salt lessens as the velocity increases. The first part of the copper salt may therefore be cooled in some cases, and its activity correspondingly reduced. This error must, I think, be small, but, so far as it exists, will always affect the results in only one direction.

We cannot therefore in this respect expect unmixed results from the experiments in tables 2 and 3, and in table 4.

The experiments in table 5 appear at first sight to be at variance with those in the other series. I offer the following hypothesis as a mode of accounting for that variation, and also of explaining all these results on velocity.



In table 5 the velocities are exactly in inverse proportion to the square of the tubes' diameters; at no other velocity is this equality of action of the active molecules of copper salt established by experiment.

The diameter or some other circumstance varying with the diameter, is therefore intimately connected with the cause, and it must be borne in mind that the action is essentially a surface action, so far, at least, as the copper salt is concerned.

I cannot use better words to convey my idea than those occurring in Roscoe's translation of Bunsen's *Gasometry*, 1857, at page 255. Bunsen is speaking of the catalytic action of platinum and oxide of manganese on peroxide of hydrogen, and his translator thus expresses his meaning,—“it is only when the products of decomposition are removed by foreign forces, such as gravitation, capillarity, expansion, &c., and by means of these *foreign* forces new matter is brought into contact, that the phenomenon is repeated.”

How then is the gas, or how are its molecules to be so brought to the surface or within its sphere or zone of action, that the same opportunities of action are offered in each of these cases? An answer to that question involves, I think, the solution of the problem.

When a stream of smoke issues from a chimney, it proceeds with a curling motion which varies with the speed of the stream. I assume that motion of that kind occurs in the interior of the chimney before the smoke escapes from it, and I regard the chimney as a tube, and infer, that in streams of gases in all tubes there must be a motion of this kind, arising from friction on the walls of the tube, and therefore varying with its diameter. In Diagram 4, fig. 1 may be supposed to represent a longitudinal section of a tube of the diameter (and surface) 2, and figs. 2, 3, and 4, similar sections of tubes of the diameter (and surface) 1, all the tubes being of the same length, and the sections all of the same thickness. Then, for convenience, using straight lines instead of curved ones, to represent the resultant motion of the molecules caused by the curling or revolving motion seen in chimney smoke, the comparative number of contacts with the active molecules of copper salt on a unit of the interior surface of the tube at different velocities, will be represented by the points of contact of the diagonal lines with the horizontal parallel lines.

In fig. 1 the molecules of gas will, as indicated, make 32 contacts on each of 2 units of active surfaces = 64 contacts in a time 4; and in fig. 4, similar molecules of gas will make 8 contacts in a time 1; the times being inversely as the velocities.

It follows that, in the case supposed in Fig. 4, in the time 4 (the same time as in fig. 1) the contacts will be  $8 \times 4 = 32$ ; or in the same time the contacts in the case Fig. 4 will be to the contacts in the case Fig. 1, as 32 is to 64, or as 1 is to 2, that is, directly as their diameters or surfaces, and if each contact be a measure of the work done, then the work done by those two tubes at the velocities given, which are in inverse proportion to the squares of their diameters, will be in direct proportion to their respective surfaces, as in the experiments. The cases represented in Figs. 2, 3 and 4 as compared together may be taken as illustrative of the principle affecting the results of experiments in table 4, viz., tubes of the same diameters and lengths with currents of gas at different velocities. When a current of liquid passes through a horizontal tube and carries with it solid and visible particles very slightly heavier than the liquid, they rest on the lower surface of the tube, and by friction on its surface rotate as the current propels them. With very low velocities, these particles simply roll along, and appear to make the same number of revolutions in traversing the same length at all velocities below some fixed rate peculiar to the particular circumstances of the experiment. At velocities higher than this particular limit, the particles both rotate and slide, and as far as observed, the rotation is constant in the same time: hence points of contact diminish in inverse proportion to the increase of velocity. A group of molecules, which in rolling round once, may bring 20 points of its circumference into contact, will revolve only half way round in half the time, and bring only half its surface-points, 10, into contact.

Or, the cause of this motion may be considered in another light. That force which tends to move the molecules from and to the surfaces of the tube, that is, diametrically, is probably a constant force, or a resultant of constant forces. Diffusion, for example, *must* perform its part in the phenomena. This diametrical motion being constant, then as the longitudinal motion, or velocity of the current varies, the resultant of the two forces may be represented by the diagonal of a

parallelogram, of which parallelogram a portion of the sides of the tube may represent the longitudinal velocity, and the diameter the constant "diametrical" force or forces. Hence Fig. 2 may be held to represent a tube with a surface 1 and a stream of gas at a velocity 1, and a diametric force 1, and showing 32 contacts on the surface 1 in the time 4.

Fig. 3 may represent a similar tube, with a velocity 2 and showing 16 contacts in a time 2. Fig. 4 represents the same tube with velocity 4 and 8 contacts in a time 1. It is also evident the quantity of gas passed will increase in equal proportion to the increased velocities, and that in each given case the number of contacts in the same time is constant. That is to say, the quantity of gas varies, but the contacts or opportunities of decomposition remain constant. Hence, if each contact does equal work, *i.e.* decomposes an equal weight of hydrochloric acid, it will follow that the same tube will yield equal weights of chlorine in the same time at all velocities, but as the quantities of hydrochloric acid passed will vary, the percentage of hydrochloric acid decomposed will decrease in inverse proportion to the quantity passed, *i.e.* to the velocity.

But the results of table 4 are in excess of this conclusion.

*Theoretical explanation of action of porous mass.*

To understand what I suggest as the cause for this difference, it is necessary, first, to consider the explanation offered for the results shown in Table 2, which for the moment may be summarised as tending to show nearly the same percentage decomposition at velocities varying within some narrow limits, and of course giving an increased quantity of chlorine from the same active molecules of copper salt, in nearly equal proportion to the increase of velocity in the passing current of gas. I regard this case also, as merely a branch of the previous one, the problem being to explain how the molecules of the gas are brought into contact with the active molecules of copper salt, or within their sphere of action, in the same numbers under the different circumstances.

If the stream of gas were a billiard ball, or a string of balls so far asunder as to allow of the motion of each ball being uninterrupted by its fellows, and the sides of the tubes and faces of the particles in the porous mass were "cushions," then the question would be answered,



if for the argument's sake, the tubes were supposed to be horizontal. For it is evident that the constant "diametric" force in the tobacco pipe or empty tube would be gravity, and as the velocity of the projectile varied, so would its angle of incidence and reflection with the tube's side vary, and the diagonals in Figs. 2, 3 and 4 would fairly represent, by straight lines, the path of two balls of the same velocity in each tube, the velocities being different in different tubes. So, too, can be easily, conceived a porous mass of particles with faces at various angles to the balls' impact. The ball would be reflected from face to face, and, irrespective of moderate variations in the velocity, the number of reflections, *i.e.* of contacts, would remain constant at all its velocities. But as its passage through the tube would at higher velocities occupy proportionately less time, the number of its contacts in the same time would increase in proportion to the increase of velocity.

This expresses the leading idea of the solution, although of course we have to do with a continuous stream of gas, and not with isolated molecules. When such a continuous stream impinges upon a surface at any angle, it is spread out into a film or sheet, the direction of which is parallel to the tangent of the point of impact, the greater part of the film flowing in the direction which makes the largest possible obtuse angle with the axis of the stream before impact. This is indicated in section in Fig. 5. A stream of gas indicated by the arrows is supposed to impinge in succession upon a series of inclined surfaces, which may be taken as roughly representing a portion of a porous mass. The course followed by the stream after contact will be the same at all the velocities now referred to. A stream of gas, however, under the supposed circumstances possesses other properties. The film referred to becomes thinner as the velocity increases, just as is the case with jets of water under similar circumstances. Regarding the layer of gas on one of the surfaces in Fig. 5 as the section of a tube, such as shown in Figs. 2, 3 or 4, if the thickness remained the same, then, as the velocity increased, the contacts would decrease at all parts of the surface, except at the point of impact; but if this thickness diminishes, then the number of contacts will increase.

There is also the case of a current passing through an interstice, not in contact with any surface during its passage. This is represented

in Fig. 6, which is supposed to be a section of the glass bulb, in which some accidentally noticed circumstances first suggested this hypothesis.

If whilst a current of gas is passing, a little vapour or smoke be introduced into it, before the bulb becomes filled and opaque, it will be noticed that the stream thickens as it crosses the space, and part of the stream strikes against the opposite surface, and is reflected along it. As the velocity of the current increases, so does the velocity of this reflex current, and in this way the contacts with the interior surface must be increased by increased velocity. There is also the other well known fact that a current of gas induces motion in the gas surrounding it, and a striking illustration of the effect of increased velocity in this respect is, I think, afforded by a gas blowpipe flame. The coal gas in the quiet air obtains its supply of oxygen from amidst superabundant oxygen and burns with a long smoky flame. A small quick current of air, containing less oxygen than its equivalent, is passed in, and the long flame drops to a short one. The velocity of the jet of air is increased and the jet again shortens. To the extent that the combustion is more perfect it may be said, more work is done in the same time, but clearly the same work is done in less space, owing to the motion imparted to the air.

Such then is the hypothesis I have to offer to account for the results shown in Tables 2 and 3. Those results would be increased, I think, if the elements of the parallel tube were wholly absent. So too the results in Table 4 would be modified and approach nearer to the ideal if the bore of the tobacco pipe were quite smooth and parallel. It is however naturally rough, and there are always little fragments of copper salt, &c, which bring more or less the result indicated in Fig. 5, *i.e.* they assimilate the two results by bringing different causes into activity. I have argued as if the particles traversed from side to side of the parallel tube at short intervals. This was merely for the sake of a convenient illustration of the principle involved, but the same argument applies equally if the motion is confined to a series of concentric cylinders moving at different velocities, quickest in the centre. Cohesion too will modify these results, as is readily conceived if a cord of many strands be imagined as replacing a stream of gas. By analogy this conception indicates a different action in a tube whether

the cord be driven or drawn. Without going further into these differences, I hope my explanation will suffice to give the leading features of the idea.

One objection to merely counting contacts, irrespective of the time of contact, is that the work done must require time, and that in so much less time a proportionately less amount of work must of necessity be completed.

Before passing to another part of the subject, I would direct attention to one view of the question of time in connection with these and similar phenomena.

Recurring to the projectile started horizontally, but under the influence of gravity. Its flight may be indefinitely short, its velocity indefinitely great, and the time of transit indefinitely brief. How small must all these elements of the problem be, so that it can be said that the projectile has not been moved by the influence of gravity? Or that the motion it has thus acquired is too small to continue until stopped by some other and equivalent force? Will it not be said that, however brief the time, a corresponding and continuing motion has been imparted? If the projectile were iron, we might substitute magnetism for gravity, and in applying the argument to other forces with corresponding objects, chemical force and its objects cannot be excepted.

I would apply the argument somewhat in this way, premising that it is merely a speculation with mechanical analogies for its support. Heat being taken as motion, and the separation of the elements of hydrochloric acid involving the idea of motion, and the particles of hydrogen and of chlorine differing in weight, it is mechanically reasonable to anticipate that a motion of hydrochloric acid, when changed by some force that is not exactly proportional to their respective weights, will tend to sever the connection between the elements. If hydrogen and chlorine were two pendulums of the same length, vibrating by the force of gravity, the change of vibration or motion would be simultaneous in the light and heavy body, but if that motion were changed by another kind of force, then the two associated bodies would diverge. Still more would an impulse



to only one of the bodies tend to their separation, and most of all a separate and contrary impulse to each. And however small the impulse were, a divergence once commenced would continue. If we now consider that heat tends to dissociate hydrochloric acid, that is, to cause such a motion of each constituent molecule that, although neither passes the bounds of stability, they approach the state of equilibrium more or less nearly, then an impulse to either, communicable like the impulse of gravity in a time indefinitely short (if indeed time be a measure applicable to the case), would cause the limits of stability to be more nearly reached or even passed by the continued motion resulting from the impulse, after the impulse itself had ceased.

Or the answer may perhaps be that in the shortest time occupied in any experiment now referred to, the limit of time was not reached. The reaction, whatever it may be, was accomplished, long before the results could be removed, and fresh material supplied. Suppositions of this kind do not admit of proof, and should at least have the support of analagous facts. Nothing occurs to me to prove that a compound of copper, or indeed any compound, can be both formed and decomposed in so brief an interval as the facts quoted would require for the adoption of this view.

4. *As to the effect of increased length of active substance.*

No. 117, Table 3, is a series of experiments made with a glass tube  $\frac{3}{4}$  in. bore filled for 3 feet of its length with fragments of fire-brick soaked with sulphate of copper. In this length were upwards of 10,000 pieces averaging  $\cdot 115$  in. in diameter, and the area of the interstices was 53% of the whole contents of the tube.

No. 53, Table 4, is a pair of experiments in which the active surface was the bore of a tobacco pipe stem  $\cdot 076$  in. in diameter and 25 ins. long. At a very moderate computation, the active surface of the fragments in the  $\frac{3}{4}$  in. glass tube was 180 times as large as in the tobacco pipe, and so far as the question of velocity or time of contact of particles of gas with the active cupreous molecules may effect the result it must be noted, that the velocity of the stream of gas over the smaller surface was at least 50 times as great as over the larger surface; yet with 2,522 fluid grains passed over the larger surface in the same time that 2,188 fluid grains passed over the smaller surface, the chlorine

obtained from the smaller surface was 84 as compared with 81 from the larger surface, *i.e.* more total work from  $\frac{1}{125}$  of the number of molecules. Looking only at the working capacity, a cupreous particle is thus proved to possess, it would seem that if this power alone were to be regarded, that the 3 feet long of active material in No. 117, Table 3, might be most materially shortened, and the same result obtained. The first surfaces must do the work, and the rest must be idle, and by increased velocity undecomposed hydrochloric acid ought to be carried to the previously inactive cupreous molecules in the rear of the tube and there be decomposed. This involves the idea of a limit of decomposition. In no case has any limit been observed, except from excess of temperature. Increased length of active substance, or longer duration of contact would always give a higher decomposition.

Tables 6 and 7 illustrate the effect of different lengths of decomposing material. The experiments recorded in No. 1, Table 6, were made in apparatus filled with continuous earthenware tubes of roughly parallel bore, in fact ordinary agricultural-drain tiles soaked in sulphate of copper of a total length of about 200 feet. Samples for analysis were drawn at the extremity and in the centre. The averaged result shows that at half the distance very nearly half the work was done. The experiments referred to in No. 2, Table 6, were performed in apparatus filled with about 100 tons of ordinary clay "marbles," about 150 feet long, the samples being drawn at the intervals marked.

These results afford only rough indications of the truth, for the temperatures in these masses always vary, and thus vitiate these results. In diagram No. 5 I have projected a curve from these results, for the sake of comparing it with others obtained on the small scale and recorded in Table 7, two of the widest range being also projected as curves on the diagram.

*Theoretical consideration, respecting increased length of active substance.*

So far as the percentage decomposed is concerned, the natural conclusion seems to be that increased length should compensate for any loss arising from increased velocity; for if increasing the velocity in a piece of apparatus, say two-fold, and thus halving the time of contact, reduces the percentage, then as doubling the length of the apparatus proportionately, preserves the time of contact, the conclusion

that similar effects must be produced appears to be inevitable. Table 6 in this way serves to confirm the different action of parallel and irregular active surfaces, No. 1 of that table showing that the work done is in simple and equal proportion to the length; whereas No. 2 shows the proportion is not simple. Table 7 gives the results of laboratory experiments, and in it are some curious results.

In the two pairs of experiments 104 and 105, making allowances for velocity, no materially different results are obtained from  $1\frac{1}{2}$  in. and 3 in. length of active fragment filling contained in a glass tube of  $\frac{1}{4}$  in. diameter. In the series 121, in a  $\frac{3}{4}$  tube at about one-eighth the preceeding velocity, the indications obtained seem to be that 16 ins. is a limit. In series 127 and 128 in a  $\frac{1}{2}$  in. tube at velocities about one-half greater than 104 and 105, and 12 times greater than in 121, the results are evidently increased up to 8 in., and if the correction in the last column in the table be accurate, an increase up to a length of 16 in. is shewn.

In the series 127 the results obtained with 4 in. and 2 in. of filling are reversed, the shorter length giving the greater results, and in (2) Table 6 a corresponding fact is noted. These are of course accidental, but illustrate the difficulties attending these experiments, and the risk that conclusions based on a limited experience may be erroneous.

The experiments on the large scale differ from the laboratory experiments much more markedly in this question of length than on any other point, for on the large scale no such results as given in 104 and 105 have been noticed.

The inferences I draw from the facts are that increased length of a porous mass with active surfaces, does not in any direct proportion compensate for increased velocity, but that the laws of each are distinct. The previous explanation as to the different action of narrow and wider tubes is probably sufficient to account for the inconsistent results evident on comparing any two of these fillings in narrow glass tubes, as the same fragments may have narrower or wider interstices from accidentally close or loose packing, and thus create a different set of circumstances in the currents of gas, causing corresponding differences in the number of contacts. But disregarding small differences, and looking at these experiments as a whole, I am unable to offer an



entirely satisfactory explanation of these results with different lengths of fragments. With parallel tubes the length increased in proportion to the velocity, does appear to maintain an equal intensity of action on the larger quantity of gas.

As possibly influencing the results of experiments with mixed streams of gases of different densities impinging upon surfaces, I would allude to the phenomena exhibited when streams of water holding in suspension particles of substances heavier than water violently impinge on surfaces. The heavier particles having the greater impulse tend to separate from the lighter stream, and streaks or clouds of these heavier particles are visible at the point of contact, when from the stream's velocity they are invisible elsewhere. Then if all ponderable matter obeys the same dynamical laws, every time that the direction of the stream is changed, and in proportion to the abruptness of the change, this separation of the heavier particles must ensue. The separation evidently must be one of degree. The stream must quickly resume its average constitution. All the particles, heavy and light, must ultimately be swept along. The elements of hydrochloric acid are in all probability held together by a stable force, that no such blow can rupture, but the mechanical hold of hydrochloric acid on oxygen or on nitrogen, or the hold of chlorine on either may not suffice, and I see no argument why it should suffice to prevent these heavier molecules in a stream of air from obeying the laws of motion obeyed by heavier particles in a stream of water. The results of direct and sudden impact, as occurring in a porous mass, may therefore differ from those of indirect, and so to say, gradual impact, occurring in parallel tubes, by affording a different opportunity for new matter to come into contact with the active surface.

The objection that the molecular motion of gaseous molecules is so considerable that the mechanical motion employed in these experiments is too small appreciably to affect the result, is, I think untenable.

The hypothesis of molecular motion involves the equality of the motion of each molecule. The lighter one moves so quickly, and the heavier one so slowly, that their "vis viva" or potential energy, is in each case exactly equal. But the second law of motion requires that a body in motion yields duly to other forces.

If therefore the normal forces of the two molecules are equal, and a fresh force affects them unequally, the effects of the normal force, being balanced, may be disregarded in considering the results of the fresh force; it may be as a very small weight in one pan of a very heavy but exquisitely delicate and equipoised balance. This illustration being rather statical than dynamical, I use it only as an experimental proof that small forces are not lost. Molecular forces must affect all my results. They are not to be ignored, but mechanical forces are active and appreciable also; my contention being for the absolute and appreciable resolution and composition of *all* natural forces which make themselves evident by motion.

6. *The effect of various proportions of Air, or of Oxygen to Hydrochloric acid.*

Recorded in Tables 8, 9, 10, and 11, are the results of the effect of various mixtures of hydrochloric acid with air and with oxygen, and of mixtures of hydrochloric acid with air compared with mixtures of hydrochloric acid with oxygen.

In Table 8 (hydrochloric acid and air) the recorded experiments vary from .31 of an equivalent to 4.44 equivalents of air to one equivalent of hydrochloric acid. The chlorine obtained per minute varies from 16 to 610 fluid grains, and the percentage decomposition from 10.8 to 86.9.

A slight examination will show that as the proportion of air increases, the percentage of hydrochloric acid decomposed increases also. There are in many of the experiments equally striking evidences that the increased dilution with air within the limits given, maintains sensibly the same weight of chlorine from the same surface in the same time.

This is also evident from the experiments in Table 9, where mixtures of hydrochloric acid and oxygen in different proportions are compared together.

In Tables 10 and 11 the action of oxygen on hydrochloric acid is compared with the action of air. Whilst the percentage results vary slightly, the greater or more intense result being on the side of air, as if the presence of nitrogen were an assistance, the quantity of

chlorine evolved is largely on the side of oxygen. In a given bulk of a mixture of hydrochloric acid and oxygen, there is more hydrochloric acid than in the same bulk of hydrochloric acid and air mixed in the same equivalent proportions. With one equivalent in each case the proportion is 1.76 in the mixture with oxygen, to 1 in the mixture with air. Two trains, composed of the relative molecules, passing the same point at the same speed, would offer opportunities of action, and might be expected to yield chlorine in proportion to the number of molecules of hydrochloric acid in equal bulks or lengths of the trains. In Table 10 the mixtures with air chance to be less than an equivalent, and comparing the actual bulk of hydrochloric acid in the gases used, the proportion is 1.63 to 1, and the quantities obtained are as 1.61 is to 1.

In Table 11 the experiments were designed to replace nitrogen with oxygen, to ascertain whether there was any specific difference in the action of the oxygen in excess. The actual average proportion is 4.85 equivalents of oxygen with one of hydrochloric acid, to one equivalent of air with one of hydrochloric acid. The proportionate quantity of hydrochloric acid in equal bulks of each is 1.03 with the oxygen to 1 with the air mixture, whilst the quantity of chlorine obtained is as 1.91 is to 1 in favour of the mixture with oxygen. The percentage results being also largely in favour of oxygen, viz., 2.28 to 1.

*Theoretical explanations of the effect of varying the proportions of the mixed gases.*

Another view should be considered before concluding that the increased quantity and intensity are due only to the resultant forces of the greater number of molecules of oxygen. If equal volumes of gases contain an equal number of molecules, then when they are mixed in equivalent proportions there must be four molecules of hydrochloric acid to one of oxygen. The following strings of symbols may represent arrangements of particles as probable as any other arrangement. Take first, the case of air and HCl, assuming for convenience that air contains 20 per cent. O and 80 per cent. N. The molecules may be arranged as follows:—first, HCl with air in equivalent proportions, thus,  $N_2, HCl, N_2, HCl, O_2, HCl, N_2, HCl, N_2$ . And secondly, HCl with O in equivalent proportions, thus,  $HCl, HCl, O_2, HCl, HCl$ , and HCl with O, to replace the N in the mixture with air, thus,  $O_2, HCl, O,$



$\text{HCl}, \text{O}_2, \text{HCl}, \text{O}_2, \text{HCl}, \text{O}_2$ . Now conceiving these to be trains passing a point of copper salt, two molecules of hydrochloric acid, may in each case be grouped with a molecule of oxygen between them, as more than enough oxygen is present in that group for both molecules of hydrochloric acid. In a train of nine molecules of this mixture with air there is one such group. In a train of molecules of hydrochloric acid and oxygen in equivalent proportions, there would be 1.76 such groups. And in the mixture where oxygen replaces nitrogen in the air mixture, there would be two such groups. The chlorine obtained by experiment is, in each of the foregoing cases, a near approximation to the theory. All intermediate mixtures will in this way give approximate results to those obtained by experiment, but not so close an approximation as the rule that the percentage of hydrochloric acid decomposed at the same temperature and velocity of gas in the same apparatus is always the same; or, that it is in proportion to the square roots of the various equivalent proportions of oxygen and hydrochloric acid. The figures obtained by dividing the percentage decomposition by the square root of  $\text{O}$  divided by  $4\text{HCl}$  are shown in the last column of most of the tables. These figures represent (on this assumption) the per centage of  $\text{HCl}$  that would be decomposed from a mixture of  $\text{HCl}$  and  $\text{O}$  in equivalent proportions, if the other conditions of the experiment were unchanged, and if the rule agreed with the experimental results, the figures in each series of experiments should be the same. The variations, therefore, show the extent of error.

Of these three suggestions, that in any piece of apparatus, at the same temperature and with the same velocity, the quantity of chlorine evolved in the same time from various mixtures of hydrochloric acid with air or with oxygen respectively, is (1) in proportion to the number of chances that molecules grouped in certain ways will strike a given point, (2) that it is uniform, and (3) that the percentage of hydrochloric acid decomposed is in proportion to the square root of the number of equivalents of oxygen to 1 of hydrochloric acid, or inversely as the square root of the equivalents of hydrochloric acid to 1 of oxygen, I dismiss the first, as its range throughout varies much the widest from experimental results. In Tables 8, 9, 10, and 11, there are 55 experiments. The results of 18 of these follow nearly equally well, the law of chances of groups of atoms or molecules

or of the square root of equivalents, but the proportions of oxygen and hydrochloric acid happen to be those at which the chances and results best agree. These 18 are merely repetitions of two sets of chances, viz., hydrochloric acid with air and with oxygen, each in nearly equivalent proportions, and hydrochloric acid with nearly five equivalents of oxygen. There are always two points where different theories, like different curves, will coincide; little importance therefore attaches to merely two points of close approximation.

*Examination of Table XII, comparing results of experiments with various mixtures of gases to ascertain the law of action.*

A comparison of the two remaining hypotheses, to which I will refer briefly, as the "equality" and "square root" hypothesis, is shown in Table 12, where the extreme errors of each hypothesis as applied to each series of experiments are averaged, the result in this form indicating that the total amount of errors in the "equality" hypothesis lie most in one direction, but the errors in the "square root" hypothesis balance each other. If instead of taking the total amount of errors, the proportion of each separate pair of errors is taken and those proportions averaged, the result is slightly in favour of the "equality" hypothesis. In the proportionate errors in this "equality" result, seven errors in excess are balanced by three errors of deficiency, whilst two experiments are correct; in the "square root" examples none are right, but the errors in excess and deficiency are equal in number. There are other ways of comparing the two sets of results, but all, I think, show too small a balance of probabilities in favour of either to determine the choice without further evidence. I may here say that our daily experiments on the large scale throw but little light on this part of the subject. The quantity of chlorine cannot be weighed or measured; it is the percentage decomposition only that can be ascertained. The "square root" hypothesis fits the facts observed fairly well, but we do not know that the "equality" hypothesis, if it were possible to apply it, would not fit the facts equally well. It would seem therefore that, pending further investigations, whilst both hypotheses are supported by experimental results, we may fairly enquire which of the two is the most rational, Both cannot be right. It is certainly remarkable that these experiments with such accidental

conditions should give rise to so many points of near accord between the two hypotheses which can only approximate for small parts of their course, as they are by no means mere arithmetical complements.

A glance at No. 119, Table 8, will show this, although the fact is really self-evident. Without stopping to ascertain the cause of this accidental coincidence, I will consider the objections to, and arguments in favour of, each hypothesis, so far as they have occurred to me. They are open to one objection in common, for they both lead pretty quickly to over 100% decomposition, although as the "equality" hypothesis leads to this the most quickly, it is the most obnoxious. As a matter of fact, the highest decomposition we have observed was 97% with one equivalent of hydrochloric acid and air. The highest recorded in these Tables is 86.9% with 2.84 equivalents of air to 1 of hydrochloric acid.

The "equality" hypothesis is also the soonest at an end in the other direction, *i.e.* when the proportion of air or oxygen diminishes, a point soon arrives at which it is completely used up, and the rule is broken. The "square root" hypothesis comes less suddenly to an end in this direction, and is therefore the more elastic of the two. Another objection is that, except in the case of a mixture of hydrochloric acid and air in exactly equivalent proportions, the proportions left as the decomposition of hydrochloric acid proceeds, must vary. For example, say 16 equivalents of oxygen are present at the commencement, to 4 of hydrochloric acid. One equivalent of the hydrochloric acid is decomposed, using one equivalent of the oxygen. There are then left 15 equivalents of oxygen to 3 equivalents of hydrochloric acid, *i.e.* a proportion of 5 to 1 instead of 4 to 1 as at the commencement; similarly a further equal decomposition, and the quantities are 14 and 2 equivalents, or 7 to 1, and the next, or 75% decomposition brings the proportion to 13 to 1. With this greater dilution the "equality" hypothesis requires an equal amount of work done. With this larger proportion of oxygen the "square root" hypothesis looks only to the proportion originally present, and looking only at intensity, that is, percentage decomposition, it says in effect, a mixture originally with 13 O to 1 HCl would act with a certain intensity, but the same mixture the result of decomposition with the products of decomposition unremoved, will act according to the pro-



portions of the original mixture, *i.e.* with a smaller intensity. Whilst I am quite unable to offer any solution of the problem if the "equality" hypothesis be correct, the "square root" hypothesis permits, I think, of explanation.

*Theoretical reasons for concluding that the action is the resultant of all the forces engaged.*

I will again turn to Roscoe's translation of Bunsen's work before quoted, page 254, for my words. "We are obliged to admit that "chemical affinity is the resultant of the attractive forces exerted by "all the molecules within the sphere of chemical attraction, whether "these molecules take part in the chemical action or not," for, he says, "the point at which the chemical attraction of the molecules is so "increased that combination can take place, is not only dependent "upon the relative attractions of the molecules undergoing combi- "nation, but also upon those particles which are present, but do not "take any active part in the decomposition."

This conclusion being not merely a speculation, but a deduction from facts, amply supported by his experiments, it cannot be restricted to those particular gases he employed. I submit that neither can it be restricted only to gases. The molecules of a gas can easily be conceived as free to act, whilst the actions of liquids and solids are more restricted, but the reaction between a gas and a solid must be free if the change does not extend to the solid. I mean this kind of action to which Bunsen alludes when referring to those molecules present which exert their force, although not taking part in the chemical action. The solid acts on the gas as much as the gas on the solid, and its force should therefore be felt in the resultant of forces as well as the forces of those molecules of gas equally near the centre of action, and which, as he says, affect the chemical action in which they do not act. In this view it is that the original mixture determines the resultant of forces from first to last. Hydrochloric acid is decomposed but water is formed. The same elementary molecules are there, and their forces remain, although differently combined. The sun does not cease to attract the moon because it is the earth's satellite, nor does a piece of iron lose its force of gravity because it is lifted and retained by a magnet against the force of gravity.

Dealing however with force as motion, another illustration will I think make this idea clearer. Take the case of two stretched vibrating strings emitting the musical notes of a chord. The sonorous motion of the air is effected by both, and becomes, so to say, the resultant of each note; different from either and yet containing both. This different motion will rouse into action strings whose motion is isochronous with either original note, and with certain energy strings whose motions form harmonics to those notes. The individuality of each note or motion is not destroyed in the resultant, although the resultant as such differs from each constituent.

As an illustration amongst many of the extent of this difference, I would refer to those figures described by a point in the circumference of a circle which revolves round its own centre whilst the circle itself revolves in a circle round another centre. I can imagine no greater difference between motions in one plane than between motion in a straight line, and in a circle. Now if in the case of the two circles just spoken of, the active circle has a diameter 1 and it revolves round a centre in a circle whose radius is 1, the motion being inverse, that is, in the contrary direction, and the velocity of the two motions such that the smaller circle's circumference would roll on the inner circumference of the larger circle, then each point of the smaller circle's circumference will describe a straight line, *i.e.* a diameter of the larger circle. And if these two circles, as a whole, form a part of a larger and more complicated arrangement of the same, or of a different kind, the motion of the points of the first circle's circumference will be the resultant of all the motions engaged, inclusive of its own. Hence the conception is possible that two chemical elements may have motions as much alike as two circles of different sizes revolving in different directions with different velocities, whilst the resultant or union of two such elements from a chemical point of view, can differ no more, I think, from the original chemical action of either element, than the mechanical conception of the motion of each of the two circles differs from that of the straight line which, when they are united in a certain way, is their resultant. And this resultant, in each such case, is not the destruction of, but is the combination of both elements, and exerts the sum of both their forces. The conclusion I infer is, that in the

experiments I have referred to, the forces due to the mixture at its commencement continue unchanged, so long as no change occurs in the proportions of the elements present. The initial resultant of the forces due to oxygen and hydrochloric acid is due to the proportions of each present, and so long as those proportions do not vary, that resultant is not varied by the different grouping of the original elements. I say initial resultant, because there is no contention that, as regards ultimate results, it makes no difference whether oxygen alone or combined with hydrogen be present in the mixture.

To recur to a former illustration. The ultimate result of the sun and moon's attraction would be different if the moon were not the earth's satellite. But the present or initial action of the sun and moon is not affected. That action is a resultant which is combined with the earth's relationship to both bodies in the total existing resultant.

The alterations of the lengths of sonorous waves of air which ensue when the vibrating origins of the waves are moved through space, and the alterations in the lengths of waves of light, which is traced to the motion of the stars emitting the light, occur to me as eminently suggestive examples of combination of forces. We can imagine the light wave accompanied by an actinic, or, I would say, a chemical wave, and the stars' motion altering the length of that wave. Without feeling that waiting or searching is *à priori* irrational, we may therefore wait for the proof that the actinic or chemical wave from one source, can be combined with mechanical motion to form a resultant wave, having the same properties as that caused by a different source whose orbit of vibration is stationary; so that different elements may, at sensible distances, cause the molecular action proper or normal to either, or to some third element or compound substance, merely by combination with mechanical motion of a suitable kind. And this of course carries with it the corollary that, as an indefinite number of forces may unite to form one resultant force, therefore, any one force may be resolved into an indefinite number of forces, so far to be called constituent, that their sum is the equal of the original.

An illustration of another kind of resultant is afforded by what is known as the balanced pendulum. The time of vibration of the whole pendulum is the resultant of the different forces of its two



parts. As these approach equality the time necessary for a complete vibration is extended. Comparing a completed vibration to a completed chemical motion (*i. e.* a formation or decomposition that can be measured), it is easy to see how two, and, so to say, opposing forces, extend the time necessary for the completion of the chemical change. To continue the analogy, we cannot in either case say when this vibration or action first begins, although we may consider this rate of motion to be indefinitely slow.

*Theoretical reasons why the action of the Copper salt should be exerted through sensible distances, i.e. in a sphere.*

It has been proved that it is the surface only of the copper salt that is active. Therefore questions of mass do not apply to it. As far as it is concerned, we have only to do with a unit or molecule of its surface. But with gases, I think, we have to deal with spheres of action, and I offer a proof of this.

Admitting the surface action of the copper salt, if the gases have not a sphere of chemical action extending through sensible distances, then action must be confined to absolute contact of molecules. This requires a solution I cannot find, to account for the varied activity of a molecule of copper salt under the different conditions of the previously mentioned experiments.

For example, there is the question of different percentages at different temperatures, when the contacts from the constancy of velocity and other conditions remain the same. These contacts may be assumed sufficient at the highest temperature to give the highest possible decomposition. The contacts remaining the same, the temperature falls, and out of the whole number of contacts that previously were operative, one half are no longer so. I can conceive no reason for this: it implies a choice. The opportunities of the whole remain equal, but only one-half are affected. If two indivisible molecules, or atoms, come into contact under equal circumstances, the action can only be confined to one by choice, which is of course a manifest absurdity.

To imagine the molecules divisible, is to grant the case, for it makes the layer of molecules in contact a sphere or zone or region of action, of which more or less is acted upon according to the temperature. The inference

I draw is, that each molecule is a centre of motion, which motion is amplified as the temperature rises. The orbit or place of motion of the molecule of copper being fixed, and the reaction only occurring when all the bodies are together, the other bodies being moveable have to be brought to the copper. And whilst the oxygen is used, and the hydrochloric acid decomposed, the copper salt remains, and is merely the medium or fulcrum of action. The motion or activity is amplified by heat, and extends through a sphere, whilst continuous spheres coalescing form a zone. All that enters within that zone is affected. It is no choice, but probably all are not equally affected, the action in the spheres decreasing from the centres to the circumferences. Within certain limits this action is sufficiently intense to overcome the bounds of stability of all the matter therein; and beyond those limits a motion may be imparted like the motion imparted by gravity to a projectile, small or large in proportion to the intensity of the action and time of its duration, although insufficient to carry the molecule beyond the limits of stability. A molecule to whose elements this amount of motion has been imparted may then enter the margin of another sphere of action, when its influence added to the previous motion will carry the atoms of the molecules beyond the bounds of stability. By this supposition it follows that *the percentage of work done by a molecule of copper upon a stream of molecules of constant velocity will depend upon the size of its sphere of action.* When this covers a larger portion of the stream, the percentage acted upon, *i. e.* decomposed, will be larger too; when the sphere is small, the percentage will be small.

*Theoretical reasons for the adoption of the "square root" hypothesis.*

But if a sphere of action exists, it must comprise the molecules within it.

The presence of the copper salt, of the oxygen, and hydrochloric acid, are all necessary to the reaction, and I have already given my reason for assuming that the copper salt molecule is only a medium or fulcrum for the other forces. So long as it and one of the other two bodies are present, in the smallest conceivable units, whether molecules or atoms, the variation of effect is produced by the variation of the proportion present of the third substance. In considering the effect on hydrochloric acid, or its decomposition, we may take the copper salt and

the hydrochloric acid in unchanged proportions, as a unit, and the variation only in the quantity of oxygen, or with equal applicability, we may take the percentage of oxygen utilised by regarding the copper salt and oxygen as a unit, and varying the hydrochloric acid. The result is the same in each case. It is more convenient, for the sake of reference to my Tables, to take the copper salt and hydrochloric acid as a unit, and to consider variations in the oxygen only, the temperature and the velocity in each case being constant.

I recur to the train of molecules for an illustration of this velocity. The train moves in each case at the same speed, but in one case there are more molecules of oxygen and fewer of hydrochloric acid than in the other case; still each molecule of hydrochloric acid is just as long in passing any given point. It is, however, subjected in the one case to the force of more equivalents of oxygen than in the other case.

Now chemical action or change is motion. The time for action being the same in each case, the ordinary law of motion will apply, viz., that the velocity will be as the square root of the force applied; that is, the velocity of chemical action, or changes, will increase as the square root of the force, that is, of the oxygen present; so that the number of the same changes occurring in the same time in each molecule or group of molecules will vary with the square root of the force, and a greater number of changes in the same molecule or group is of course a greater percentage decomposition.

*Theoretical inferences from experiments with mixtures of Air and of Oxygen.*

This idea of a sphere of action and of the resultant of forces also implies more or less of an idea of "transparency" of matter to force. The same idea is also suggested by the results in Table 10, comparing the action of oxygen and of air. Nitrogen must be "transparent" to the force of oxygen. The percentage action when nitrogen is present is a little the larger. This may be that nitrogen assists specifically, or that it is a diluent to oxygen and hydrochloric acid and so attenuates them, and the molecules may act more freely when attenuated. All this seems to necessitate more or less of mutual penetrability of gaseous



matter. This may be merely the rapid motion of all the molecules in all directions across each others' orbits, so that every point in the space occupied will in the course of an exceedingly brief interval be visited by different particles of each gas present. Without offering any opinion on the constitution of matter, I employ the words atom and molecule only as symbols on which to fix the thought. Figures are merely symbols for numbers, and yet symbols, which having nothing in common with numbers, are our guides in the use and comprehension of the power of numbers. I would be understood as using the words referred to in a similar sense.

### *Conclusions.*

Reviewing the results of all the experiments contained in the Tables in the lights I have endeavoured to explain, I arrive at the following conclusions:—

1. That with the same mixture of gases, and at the same temperature, the amount of hydrochloric acid decomposed by the aid of a molecule of the copper salt in a given time, depends upon the number of times the molecules of the mixed gases are passed through the sphere of action of the copper salt. Conversely, that the activity of a molecule of copper salt depends upon the speed with which fresh matter is presented to, and the products are removed from it. Not that force is in this way created, but again using Bunsen's words (page 255 of the work quoted) "catalytic action is not an equivalent to an unlimited amount of labour, but for every decomposition effected, an equivalent amount of force is absorbed, just as in the case of a weight raised by a falling body, a force is expended exactly equivalent to the work done."

2. That in long parallel tubes of the same diameter, the number of opportunities of action in the same time is nearly the same at all velocities of the current of gas.

3. That in long parallel tubes of different diameters, the number of opportunities of action of each molecule of copper salt is the same when the velocities of the currents of gas are in inverse proportion to the squares of the tubes' diameters.

4. That in porous masses the opportunities of action increase with increased velocities of the current of gas in nearly direct proportion.

5. That, other conditions remaining the same, the percentage of hydrochloric acid decomposed in any given time varies with the square root of the proportionate volume of oxygen to hydrochloric acid. Conversely of course, the percentage of oxygen used varies with the square root of the proportionate volume of hydrochloric acid to oxygen.

6. That the cupric chloride formed bears no definite proportion to the quantity of chlorine produced.

7. That as the sphere of action includes molecules not in contact with the copper salt, therefore hydrochloric acid must be decomposed under circumstances where the union of either element with the copper salt is impossible, *i.e.* that the decomposition must in part, if not entirely, be caused by the resultant of the forces engaged, and therefore direct from  $2\text{HCl} + \text{O}$  to  $\text{H}_2\text{O} + 2\text{Cl}$ .

Imperfections in my work must have been already sufficiently evident, and there are two points in particular where further experiment is necessary, *viz.*, as to the utmost limit of decomposition at different temperatures and with different mixtures, and as to the value of increased length of apparatus of different kinds.

Still, despite the incompleteness of my attempts, it is I think abundantly evident that results of the kind shown in these experiments cannot be restricted to mixtures of hydrochloric acid and air or oxygen reacting in the presence of copper salts, &c. They must be capable of very general application to problems in chemical dynamics. When liquids act on solids, for example, and currents or motions in the liquids become perceptible, the phenomena of streams must occur, varied according to the varied circumstances of each case. The amount of chemical change occurring in any given time is not merely a measure of the chemical force engaged, but is in reality a resultant of all the forces engaged, physical and mechanical as well as chemical; and in estimating the difference between chemical forces, those which Bunsen calls "foreign forces" must first be eliminated from the result. I trust

my efforts in this direction will be only a prelude to a full generalisation by abler hands.

I wish with your permission, before I conclude, to record my thanks to my partners for their forbearance during the four years and upwards that this research has extended. All the resources of our establishment have been freely at my disposal. Next, I would acknowledge the assistance throughout, of our laboratory chief, Dr. F. Hurter, and of my late lamented chief assistant, Mr. W. R. Jekyll, Daltonian Scholar of Owen's College; and latterly I have had the valuable assistance of Mr. Rocholl, who has worked with the large brick furnace and cast iron tube I have described.



**TABLE A.**  
**PRELIMINARY TEST EXPERIMENTS. (PIECES.)**

Reference No.	Date.	Time.	Duration in minutes.	HCl passed in grains.	Cl obtained in grains.	% HCl decomposed.	
1	1871 Jan. 17	P.M. 4 : 53 — 5 : 25'75	32'75	99'8	57'51	59'3	Tube laid in thin sheet iron gutter.
		5 : 37'5 — 6 : 9'5	32'00	100'0	57'58	59'1	
2	Jan. 18	A.M. 11 : 33 — 12 : 3'5	30'50	107'31	47'92	45'8	Ditto.
		P.M. 12 : 13 — 12 : 43'25	30'25	109'50	48'15	45'1	
3	Jan. 18	4 : 46 — 5 : 16'25	30'25	104'46	44'51	43'7	Ditto.
		5 : 25'75 — 5 : 56	30'25	105'98	45'58	44'1	
4	Jan. 19	12 : 15'75 — 12 : 46'25	30'50	108'18	56'23	53'2	Same tube shaken up and cleaned outside from deposited carbon.
		12 : 55'5 — 1 : 27'75	32'25	104'02	55'91	54'6	
5	Jan. 19	3 : 32'75 — 4 : 3'5	30'75	111'25	42'60	39'6	Same tube.
		5 : 9'5 — 5 : 40'75	31'25	111'03	41'32	38'6	
6	Jan. 21	A.M. 11 : 8'75 — 11 : 37	28'25	103'80	66'28	65'6	New tube inserted in iron gas tube instead of being laid in iron gutter.
		P.M. 12 : 43'75 — 1 : 11	27'25	102'27	67'20	67'4	
7	Jan. 23	A.M. 10 : 41'5 — 11 : 8'75	27'25	113'44	62'30	56'4	Same tube.
		11 : 27'75 — 12'0	32'25	114'70	28'9	25'6	
8	Jan. 23	P.M. 2 : 56 — 3 : 27'25	31'25	109'72	58'0	54'3	Ditto.
		3 : 21'5 — 3 : 51'25	29'75	109'50	58'5	54'9	
9	Jan. 24	A.M. 10 : 15 — 10 : 45'75	30'75	111'03	69'75	64'6	Ditto.
		P.M. 11 : 45 — 12 : 15'25	30'25	114'97	72'63	64'9	

TABLE I.

## DIFFERENT TEMPERATURES.

	No.	O to 4 H Cl.	Velocity.	Fluid grains of Cl. obtained.	o/o of H Cl.	Temperature.
			Fluid Grains per Minute.	Per Minute.	Decomposed.	Degrees Fahrenheit by Pyrometer.
Pieces of Fire-brick Saturated with Cu. SO <sub>4</sub> $\frac{1}{16}$ in. tube.	73			0.0	0.0	643
	72	1.44	1898	5.8	1.5	712
	71	1.66	1965	13.3	3.6	712
	74	1.46	2250	128.5	28.1	855
	76	1.37	1902	271.8	66.2	928
	75	1.27	2060	300.0	66.1	952
	77	1.18	2033	285.3	61.2	1027
Pieces of Fire-brick with Cu. SO <sub>4</sub> $\frac{1}{16}$ in. tube.	78			0.0	0.0	590
	79	1.14	1741	4.5	1.1	695
	80	1.43	2196	77.7	17.2	800
	86	1.44	1970	79.9	19.8	810
	82	1.26	1903	60.7	14.4	822
	85	1.48	2131	257.3	59.9	857
	87	1.25	1767	246.6	62.8	876
	81	1.14	2322	342.8	63.2	915
	83	1.31	2061	284.1	63.7	936
	84	1.49	1922	219.2	56.8	995
Pieces of pure Cu. SO <sub>4</sub> $\frac{1}{16}$ in. tube.	96a	1.44	1680	2.7	.8	715
	99a	1.00	1848	14.8	3.2	737
	100a	1.16	1738	29.8	7.4	760
	97a	1.14	1781	45.7	11.0	800
	98a	1.21	1919	108.5	25.0	852
	101a	.83	1631	278.8	62.6	875
Marbles Saturated with Cu. Cl <sub>2</sub> $\frac{1}{16}$ in. tube.	105	2.19	2770	142.0	32.8	707
	104	2.28	2547	154.9	39.9	725
	99b	1.00	2380	302.8	50.9	737
	100b	1.16	2202	341.0	66.9	760
	102b	1.22	1400	217.5	69.0	820
	103	1.22	1765	216.2	54.4	837
	101b	.83	3345	410.3	44.9	875

**TABLE II.**  
DIFFERENT VELOCITIES.                      PIECES.

	O to 4 HCl.	Velocity.	RATIOS.	Temperature.		Fluid grains of Cl. per Minute.	o/o of HCl. decomposed.
		Fluid Grains per Minute.		Degrees Fah- renheit by Pyrometer.	Readings of Galvanometer		
No. 111 ...	1'68	820	1'	940		82	60'0
(2'3)	1'82	2013	2'45	930		195	61'5
1/2 in. tube							
No. 117 ...	1'35	191	1'	820	54'8	16	42'9
(1'2)	1'42	332	1'74	825	54'8	27	43'4
3/4 in. tube							
No. 118 ...	1'76	241	1'	950	60'0	32	74'9
(1'2)	1'74	551	2'30	940	60'0	71	71'0
1/2 in. tube							
No. 127 ...	1'22	753	1'	910	72'6	32	18'7
(2'3)	1'20	1350	1'79	910	72'6	37	12'1
1 1/4 in. tube							
No. 131 ...	1'32	184	1'	950	70'1	23	55'4
(1'2)	1'21	504	2'70	950	70'4	71	32'6
1/2 in. tube							
No. 30.....	1'14	3217	1'			208	31'9
	1'17	5231	1'62			321	30'9
No. 31.....	1'12	5595	1'			359	31'3
	1'07	6918	1'23			477	32'9
No. 32.....	1'03	5147	1'			458	41'6
	1'01	10370	2'01			1118	49'8
No. 33.....	1'06	4987	1'			683	65'0
	1'01	10210	2'05			1259	56'2
No. 34.....	1'17	5957	1'			658	55'6
	1'13	14250	2'40			1178	40'6
No. 35.....	1'08	5170	1'			570	54'4
	1'07	7518	1'45			809	52'9
No. 64.....	1'04	2680	1'			290	51'4
	1'07	5026	1'88			478	45'67
No. 65.....	1'02	2680	1'			256	45'3
	1'04	5026	1'88			480	39'0
			25'50			3667 6521	628'4 568'57
		Averages	1' : 1'96			282'1 501'6	48'34 43'74
						1' : 1'78	1' : '9



TABLE III.

DIFFERENT VELOCITIES.—PIECES.

		O to 4 HCl.	VELOCITY.		TEMPERATURE.		Fluid Grains of Cl. per minute.	o/o of HCl. decom- posed.	
			Fluid Grains per Minute.	RATIOS.		Degrees Fahren- heit by Pyro- meter.			Readings of Galva- nometer.
				Direct.	In- verse.				
No. 117 ...	1	1'35	191	1'	52'4	820	54'8	16	42'9
$\frac{3}{4}$ in. tube	2	1'42	332	1'74	30'2	825	54'8	27	43'4
	3*	1'26	695	3'63	14'5	800	54'0	40	28'4
	4*	1'18	1602	8'38	6'2	810	54'8	51	15'2
	5*	1'25	2522	13'20	4'	820	54'8	81	16'0
	6*	1'19	10028	52'40	1'	820	54'8	149	7'2
No. 118...	1	1'48	241	1'	43'	950	60'	32	74'9
$\frac{3}{4}$ in. tube	2	1'46	551	2'3	18'	940	60'	71	71'0
	3	1'28	2735	11'3	3'8	955	60'	332	61'4
	4	1'25	3545	14'7	2'9	940	60'	403	56'6
	5	1'23	10399	43'	1'	955	60'	743	35'3
No. 131...	1	1'11	184	1'	13'8	950	70'1	23	55'4
$\frac{1}{2}$ in. tube	2	1'01	504	2'7	5'1	950	70'4	71	32'6
	3	1'14	2527	13'8	1'	950	69'8	121	22'6
No. 111...	2	1'68	820	1'	7'90	940		82	60'0
$\frac{1}{2}$ in. tube	3	1'82	2013	2'54	3'1	930		195	61'5
	4	1'93	6235	7'90	1'	930		553	58'3

**TABLE IV.**  
DIFFERENT VELOCITIES.—PIPES OF EQUAL BORE.

O to $\frac{1}{4}$ HCl.		VELOCITY.					
		Fluid Grains per Minute.	Ratios in each set of Experiments.	Fluid Grains of Cl. obtained per Minute.	o/o of H Cl. decomposed.	o/o of HCl. decomposed.	$\sqrt{\frac{O}{4 \text{ HCl.}}}$
No. 50.....	1'22	2159	1'	99	23'75	21'5	
'117 tube...	'95	5744	2'66	161	12'70	13'1	
No. 51.....	1'26	2203	1'	107	26'30	23'4	
'117 tube...	1'04	5106	2'23	125	11'80	11'6	
No. 53.....	1'12	2188	1'	84	18'82	17'8	
'076 tube...	'91	4347	1'99	99	10'20	10'7	
			6'88	290 385	68'87 34'7	62'7 35'4	
			1' : 2'29	96'6 128'3	22'96 11'6	20'9 11'8	
				1' : 1'33	1' : '5	1' : '56	

**TABLE V.**  
DIFFERENT VELOCITIES.—PIPES OF DIFFERENT BORE  
RATIO OF DIAMETERS 1 : 1'54.  
Do. SECTIONS 1 : 2'38.

O to $\frac{1}{4}$ HCl.		VELOCITY.					
		Fluid Grains per Minute.	Ratios in each set of Experiments	Fluid Grains of Cl. obtained per Minute.	o/o of HCl. decomposed.	o/o of HCl. decomposed.	$\sqrt{\frac{O}{4 \text{ HCl.}}}$
No. 46, Large	1'60	4467	1'	137	18'80	14'9	
Small	1'45	4467	2'38	80	10'30	8'6	
Small	1'55	4467	2'38	80	10'80	8'7	
No. 48, Large	1'25	4663	1'	161	18'05	16'1	
Small	'98	4531	2'31	116	11'45	11'6	
No. 49, Large	1'16	4596	1'	114	12'47	11'6	
Small	1'09	4731	2'45	83	8'63	8'3	
			9'52	412 359	49'32 41'18	42'6 37'2	
<i>Averages..</i>			1' 2'38	137'3 89'75	16'44 10'3	14'2 9'3	
				1'53 : 1'	1'59 : 1'	1'527 : 1'	

Large = '117 ins. dia.  
Small = '076 ins. dia.

**TABLE VI.**  
DIFFERENT LENGTHS OF DECOMPOSING MATERIAL.  
EXPERIMENTS ON A LARGE SCALE.

I. DECOMPOSER WITH DRAIN TILES.

o/o of HCl. decomposed.

By one-half.	By the whole.
16.6	30.3
12.2	30.6
12.4	30.6
7.1	18.5
10.3	16.9
9.9	23.5
10.8	21.6
14.5	25.7
93.8	197.7
<i>Av.</i> 11.7	24.7

II. DECOMPOSER WITH MARBLES.

o/o of HCl. decomposed after passing through.

1-tenth.	3-tenths.	5-tenths.	7-tenths.	9-tenths.	All.
1.8	19.6	42.9	41.5		
	27.6	57.6	64.5		72.1
			41.8	52.2	63.9
				42.3	46.5

**TABLE VII.**

DIFFERENT LENGTHS OF PIECES OF DECOMPOSING  
MATERIAL IN GLASS TUBES.

			O to 4 HCl.	Velocity.	Temperature.				o/o of HCl. decomposed.
	Length of material in inches.	Ratios.		Fluid grains per minute.	Degs. Fah. by Pyro- meter.	Readings of Galvano- meter.	Fluid grains of Cl per minute.	o/o of HCl. decom- posed.	$\sqrt{\frac{O}{4 \text{ HCl.}}}$
104 $\frac{1}{2}$ tube.	3	2	2.28	2547	725		136	39.9	24.2
	$1\frac{1}{2}$	1	2.28	3337	725		138	31.6	19.2
105 $\frac{1}{2}$ tube.	3	2	2.19	2770	707		125	32.8	20.3
	$1\frac{1}{2}$	1	2.19	2920	707		123	30.6	18.9
121 $\frac{3}{4}$ tube.	24	3	1.15	800	900		30.5	21.	17.9
	16	2	.96	710	905		31.5	19.9	18.5
	8	1	.93	712	905		28.	18.6	17.7
127 $\frac{1}{4}$ tube.	16	32	.99	973	890	72.3	42	18.7	17.1
	8	16	1.09	743	906	72.5	31	19.	16.8
	4	8	1.05	954	905	72.5	22	10.2	9.0
	2	4	1.05	905	900	72.5	27	13.6	12.0
	1	2	1.11	860	900	72.5	17	9.1	7.9
	$\frac{1}{2}$	1	1.09	729	903	72.4	12	7.9	6.9
128 $\frac{1}{4}$ tube.	8	16	1.73	982	965	75.	54	34.1	23.7
	2	4	1.78	819	950	75.	47	31.2	21.4
	1	2	1.76	684	960	75.1	26	20.	13.8
	$\frac{1}{2}$	1	1.78	747	965	75.2	18	15.8	10.9



TABLE VIII.

DIFFERENT MIXTURES—HCl. AND AIR—(PIECES.)

	O to 4 HCl.	Velocity.	TEMPERATURE.		Fluid grs. of Cl per minute.	o/o of HCl decomposed.	o/o of HCl decomposed.	
			Fluid Grains per Minute.	Degrees Fahrenheit by Pyrometer.			Readings of Galvanometer.	$\sqrt{\frac{O}{4 \text{ HCl.}}}$
No. 129	1	1'87	822	885	70'8	26	25'8	18'7
1/2 in. tube...	2	2'43	776	885	70'8	31	31'8	20'4
	3	2'87	1005	885	70'7	36	31'7	18'6
	4	3'04	744	885	70'6	26	33'3	18'9
	5	4'44	764	880	70'6	23	39'3	18'6
No. 132	1	1'83	950	850	63'7	16	10'9	7'4
1/2 in. tube...	2	1'94	1011	850	63'7	17	10'8	7'1
	3	2'58	975	850	63'7	16	13'5	7'7
	4	2'78	1002	850	63'7	17	14'9	8'2
No. 133	3	1'36	858	940	69'6	67	40'9	34'9
1/2 in. tube...	4	1'46	978	940	69'8	73	41'3	34'1
	5	1'74	922	940	69'9	74	49'2	31'9
No. 119	3	1'11	1767	830	55'5	99	26'2	24'9
1/2 in. tube...	4	1'87	1660	830	55'5	103	40'3	29'5
Galvano-meter wire inside tube.	5	2'84	1633	830	55'5	112	60'5	35'9
	6	2'92	1569	830	55'5	109	62'0	36'3
	7	3'43	1681	830	55'5	114	69'1	37'3
	8	4'28	1612	830	55'5	111	83'8	40'5
No. 10.....	1	'99	5317			601	51'4	51'8
	2	2'84	5096			484	86'9	51'7
	3	2'80	4987			446	81'1	48'5
No. 11.....	1	1'03	5026			610	56'2	55'5
	2	2'60	5261			478	77'3	48'2
	3	2'69	5106			431	73'7	45'1
					(Pipes)			
No. 137	1	'72	956		67'7	32	12'3	14'4
1/102 tube...	2	'96	1018		67'7	37	14'8	15'0
	3	1'33	1040		67'7	35	17'1	14'8
No. 54	1	1'26	4595			136	15'8	14'1
1/117 tube...	2	2'97	4731			135	27'6	16'0
No. 55	1	1'09	4731			141	14'7	14'4
1/117 tube...	2	2'60	4662			140	26'2	16'2
No. 67.....	1	'92	4436			159	14'9	15'5
1/117 tube...	2	'31	4501			127	7'7	13'7

TABLE IX.

DIFFERENT MIXTURES—HCl. AND O—(PIPES.)

	O to 4 HCl.	Velocity.	TEMPERATURE.		Fluid Grains of Cl. per Minute.	o/o of HCl. decomposed.	o/o of HCl. Decomposed.
			Degrees Fahrenheit by Pyrometer.	Readings of Galvanometer.			$\sqrt{\frac{O}{4 \text{ HCl.}}}$
No. 62 117 tube...	1'73	4248			305	21'8	16'6
	3'13	4270			335	27'8	15'7
No. 63 117 tube...	1'92	4311			310	22'6	16'9
	3'52	4222			326	30'7	16'3

TABLE X.

MIXTURES WITH AIR AND WITH O. (PIPES.)

	O to 4 HCl.		V'locity	Fluid grains per minute.	Fluid grains of Cl. per minute.	o/o of HCl. decomposed.	o/o of HCl. decomposed.
							$\sqrt{\frac{O}{4 \text{ HCl.}}}$
No. 56. 117 tube	1'27	Oxygen.	4705	158	9'8		8'7
	1'02	Air .....	4770	115	11'9		11'8
No. 57. 117 tube	1'04	Oxygen.	4750	178	10'2		10'0
	'96	Air .....	4840	118	11'3		11'6
No. 60. 117 tube	1'12	Oxygen.	4352	247	15'3		14'4
	1'	Air .....	4505	163	16'8		16'77
No. 61. 076 tube	1'03	Oxygen.	4221	254	16'2		16'0
	'98	Air .....	4350	168	17'6		17'8
No. 63. 117 tube	1'92	Oxygen.	4311	310	22'6		16'2
	1'92	Air .....	4408	156	24'6		17'7
No. 37.	1'13	Oxygen.	4863	942	57'0		53'7
	'913	Air .....	4662	594	55'5		58'1
No. 38.	1'12	Oxygen.	4531	790	46'4		43'9
	'83	Air .....	4596	468	42'4		46'5
Averages	8'63	7'623		2879	1782	177'5	180'1
	1'23	1'089		411'3	254'5	25'3	25'7
	1' :	'87		1'61 :	1'		1' : 1'11

**TABLE XI.**  
MIXTURES WITH AIR AND WITH O.

	O to 4 HCl.		V'locity			o/o of HCl. decomposed.
			Fluid grains per minute.	Fluid grains of Cl. per minute.	o/o of HCl. decomposed.	$\sqrt{\frac{O}{4 \text{ HCl.}}}$
No. 58. "117tube	4'75	Oxygen.	4662	265	26'7	12'2
	1'04	Air .....	4845	115	11'2	11'0
No. 59. "117tube	5'081	Oxygen.	4845	268	35'7	15'8
	'986	Air .....	4663	163	16'2	16'3
	9'831 2'026			533 278	62'4 27'4	28'0 27'3
Averages	4'915 1'013			266'5 139	31'2 13'7	14' 13'6
	4'85 : 1'			1'91 : 1'		1'03 : 1'

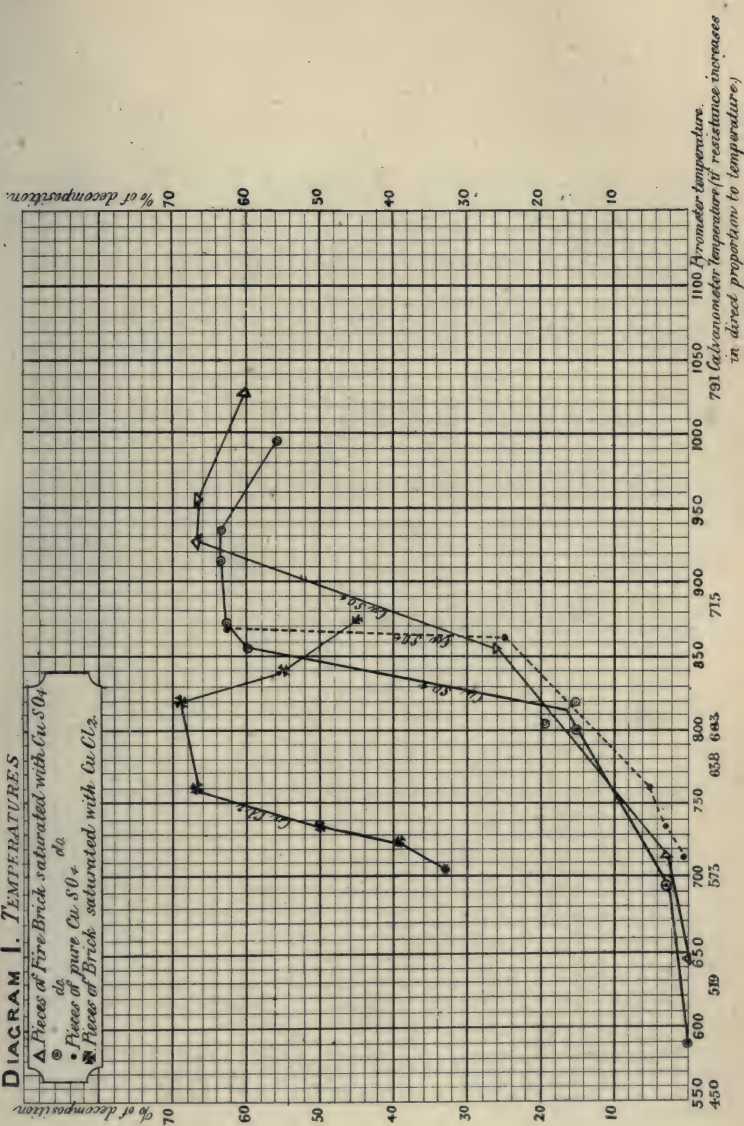
**TABLE XII.**

Comparison of the extreme errors of the "equality" and "square root" hypotheses applied to each series of experiments. The widest variations in each series are chosen, the experiment with the smaller proportion of oxygen being to the left hand.

Reference No.	"Equality" result. Quantity of Cl.				"Square root." o/o decomposition.			
	Least O.	Most O.	Least O.	Most O.	Least O.	Most O.	Least O.	Most O.
129	36	23	::	1' : '64	20'4	18'6	::	1' : '91
132	16	17	::	1' : 1'06	7'1	8'2	::	1' : 1'15
133	67	74	::	1' : 1'10	34'9	31'9	::	1' : '91
119	99	114	::	1' : 1'15	24'9	40'5	::	1' : 1'63
10	601	446	::	1' : '74	51'8	48'5	::	1' : '94
11	610	431	::	1' : '71	55'5	45'1	::	1' : '81
137	32	37	::	1' : 1'16	14'4	15'0	::	1' : 1'04
54	136	135	::	1' : 1'0	14'1	16'0	::	1' : 1'13
55	141	140	::	1' : 1'0	14'4	16'2	::	1' : 1'12
62	305	335	::	1' : 1'1	16'6	15'7	::	1' : '95
63	310	326	::	1' : 1'05	16'9	16'3	::	1' : '96
67	127	159	::	1' : 1'25	13'7	15'5	::	1' : 1'13
Averages	206'6	186'4		1' : 1'	23'7	23'9		1' : 1'05
	1' : '9				1' : 1'01			

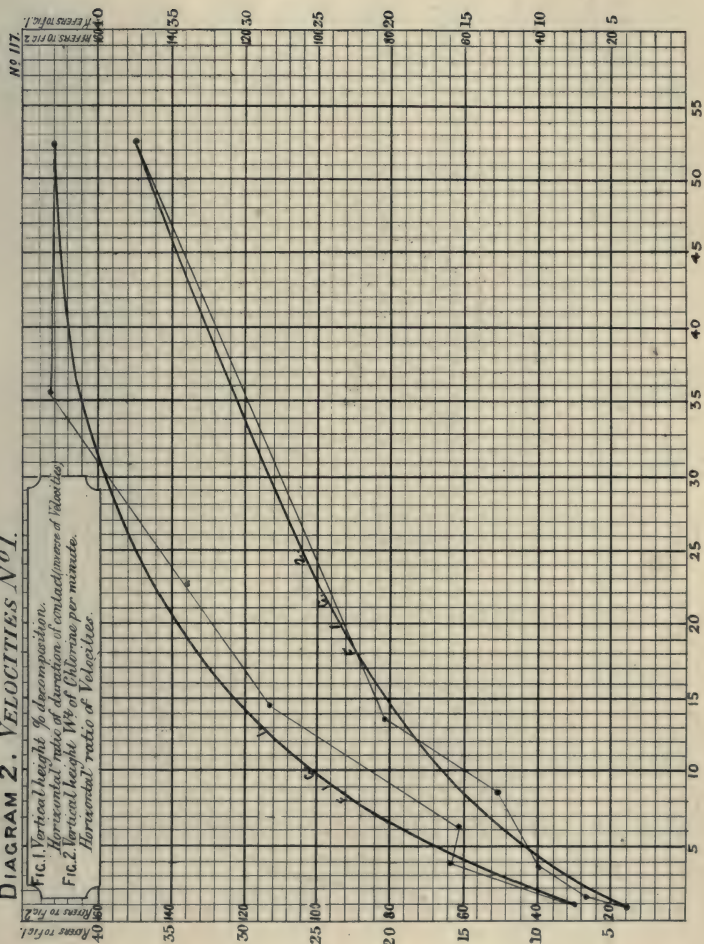


DIAGRAM I. TEMPERATURES





# DIAGRAM 2. VELOCITIES No. 1.

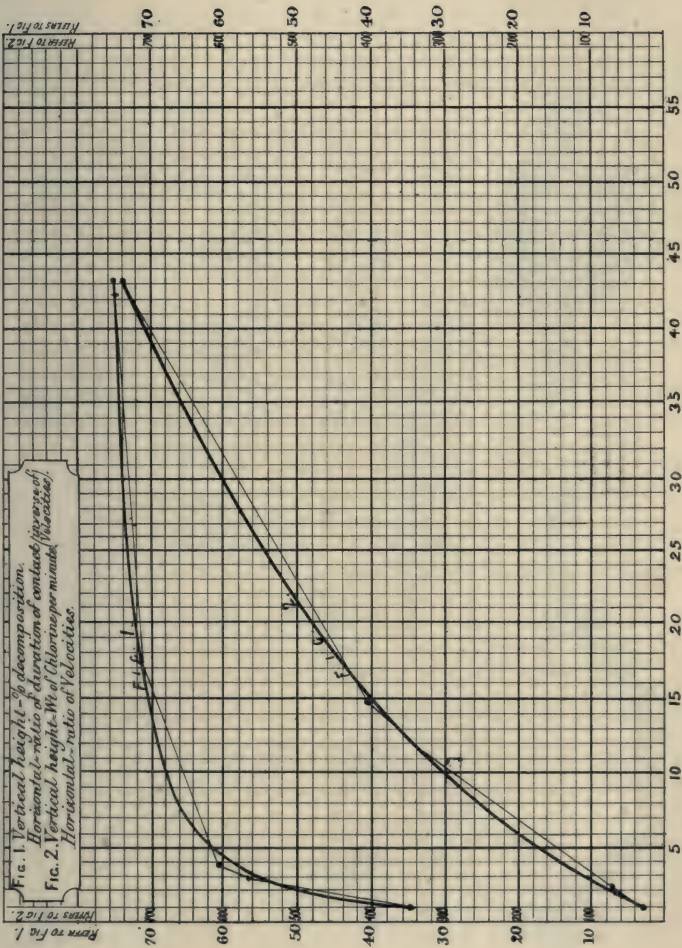






# DIAGRAM 3. VELOCITIES No 2.

No 118.







# DIAGRAM 4.

FIG. 1.  
Surface 2. Velocity 1. Contacts per unit of surface 32.

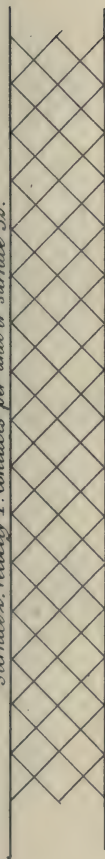


FIG. 2.  
Surface 2. Velocity 1. Contacts 32.



FIG. 3.  
Surface 1. Velocity 2. Contacts 16.

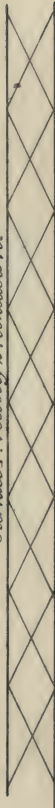


FIG. 4.  
Surface 1. Velocity 4. Contacts 8.

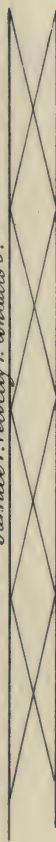
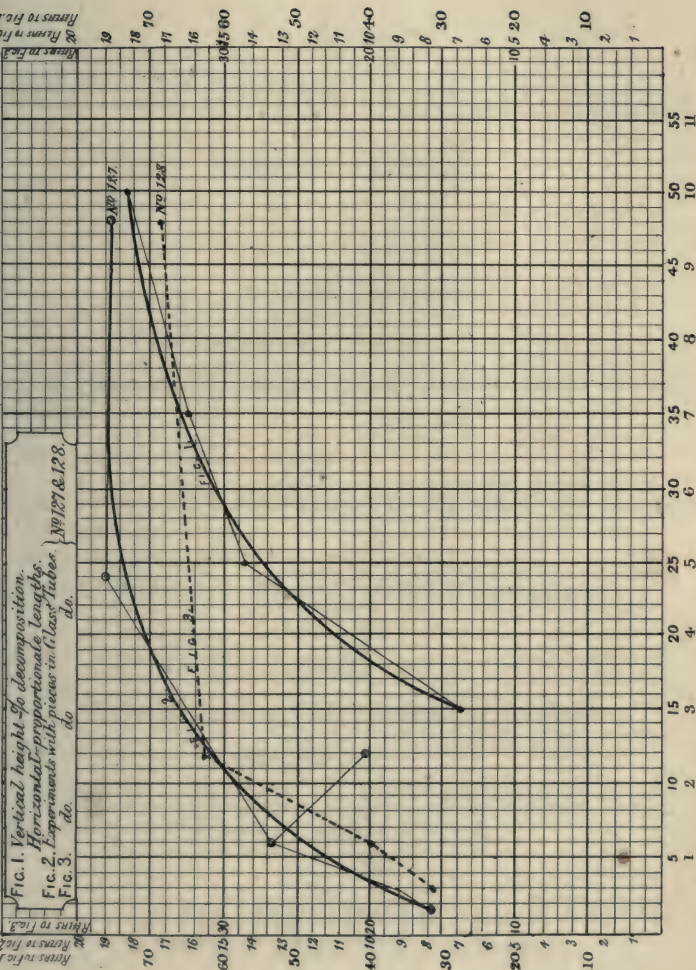


FIG. 5.

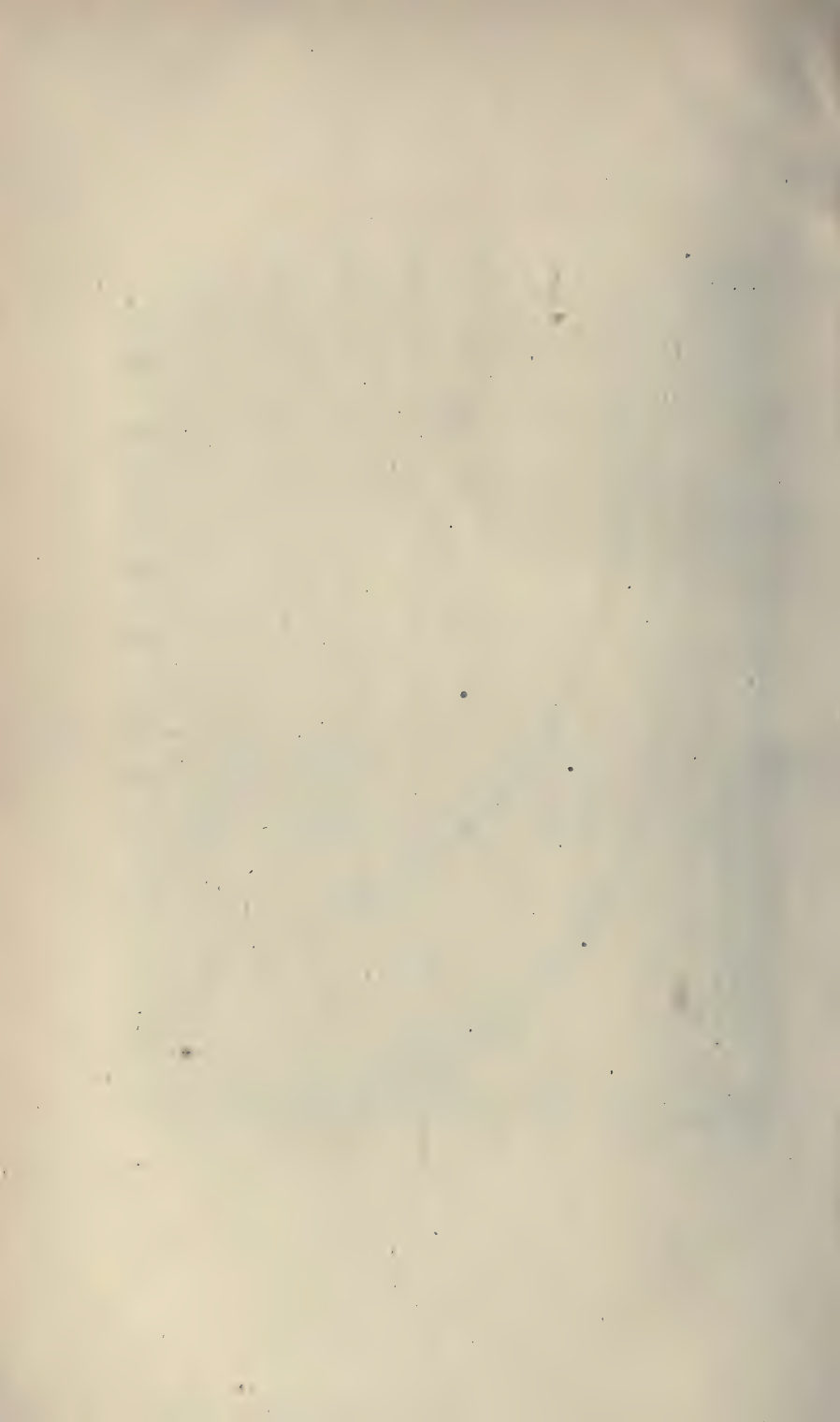
FIG. 6.



# DIAGRAM 5. DIFFERENT LENGTHS OF DECOMPOSING MATERIALS.







## PROCEEDINGS

AT THE

## MEETINGS OF THE CHEMICAL SOCIETY.

SESSION 1871-72.

November 2nd, 1871.

Dr. Frankland, President, in the Chair.

Mr. R. Gerstl, University College, was duly elected a Fellow of the Society.

The following papers were read :—

“On a Process for the Estimation of Fluorine:” by Mr. Archibald Liversidge.

“On Anthraflavic Acid:” by Mr. W. H. Perkin.

“On the Distillation of Wood:” by Mr. Watson Smith.

November 16th.

Professor Odling, Vice-President, in the Chair.

The following papers were read :—

“On Burnt Iron and Steel:” by Mr. W. H. Johnson, B.Sc.

“On an Improved Siphon:” by Mr. F. Hart.

December 7th.

Dr. Frankland, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

Charles Thomas Woodcote, Stoke Bishop; Benjamin Tanner, Liverpool; Hugh Paterson, Warrington, Cumberland; Frederick Hicks, Magdalen College, Oxford; George Joseph Warner, Manchester; William John Wilson, Great Portland Street, W.;

William Gray, Blackheath Park; Robert Irvine, Leith, N.B.; Reginald C. Woodcock, Durham; Donald Munro, Glasgow.

The following papers were read:—

"On Essential Oils," Part II: by Dr. J. H. Gladstone.

"Observations on Nitrochlorophenols:" by Dr. H. E. Armstrong.

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December 21st.

Dr. Williamson, Vice-President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

William W. Abney, Rochester, Kent; Jonathan Ingle Calvert, Lancashire; Christopher Childs, 4, Oxford Terrace, Hyde Park; Frederick Montague Page, Lisle Street, Leicester Square.

The following papers were read:—

"On Eulyte and Dyslyte:" by Mr. H. Bassett.

"On the Nitration-products of Dichlorophenol-sulphonic Acids," No. IV: by Dr. H. E. Armstrong.

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January 18th, 1872.

Dr. Frankland, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

Julian Louis Vanderstraaten; Keppell Street, Russell Square; John Millar Thompson, King's College; Charles W. Vincent, Royal Institution; Robert Barton, Melbourne; David Watson, Washington, Co. Durham; William Thompson, Royal Institution, Manchester; William Forster, Arundel Street, Haymarket; Henry James Helm, Forest Hill; Thomas W. Fletcher, Warrington; George Thomas Glover, Belfast; Thomas Eltoft, Haverstock Hill.

Mr. D. Howard read a paper "On Quinine."

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February 1st.

Dr. Frankland, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

William H. Chandler, Pennsylvania; Charles F. Chandler,



New York; Benjamin P. Medcalf, Coleman Street; John Watts, Royal Institution.

The following papers were read :—

“On the Crystalline principle of Barbadoes Aloes :” by Dr. W. A. Tilden.

“On the Relation between the Atomic Hypothesis and the Condensed Symbolic Expression of Chemical Facts and Changes known as Dissected (Structural) Formulæ :” by Dr. C. R. A. Wright.

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February 15th.

Dr. Frankland, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society :—

Ludwig Mored, Farnworth, Warrington; Edward Kinch, Royal Agricultural College, Cirencester; Edward Packard, Jun., Bramford, Ipswich; John Ruffle, Plaistow, Essex; Frederick John Barrett, Wolverhampton; Edward Handfield Morton, Newport; Ross Scott, Bayswater.

Dr. Roscoe gave an account of his researches on the compounds of Tungsten.

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March 7th.

Dr. Debus, Vice-President, in the Chair.

The following gentlemen were duly elected Fellows of the Society :—

Henry Baden Pritchard, Royal Arsenal, Woolwich; James Ballantyne Hannay, Glasgow; J. Vincent Taylor, Westminster; George Smithers Packer, New Cross; Robert William Atkinson, University College; Walter William Fischer, Corpus Christi College, Oxford.

The following papers were read :—

“On the Reduction of Ethylic Oxalate by Sodium Amalgam :” by Dr. Debus.

“On Metastannic Acid and the Detection and Estimation of Tin :” by Mr. A. H. Allen.

“Note on the quantity of Cæsium contained in the Water of the Hot Spring found in Wheal Clifford :” by Col. Philip Yorke.

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March 21st.

Prof. Odling, Vice-President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

George Atwood, San Francisco; Edward Northway Butt, Curzon Street, Mayfair; William Moss Bouron, Stockton-on-Tees.

A paper was read "On the Non-existence of the Hyponitrous Acid discovered by Dr. Divers:" by M. Maumené.

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March 30th.

Anniversary Meeting. (See page 341.)

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April 4th.

Dr. Frankland, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

William Frederick Donkin, Oxford; Charles D. Hunter, Bridge of Allan, N.B.; Reginald Le Neve Foster, Bradford, Manchester; Alexander Noble, Glasgow; W. Little, Lincolnshire; William Henry Walbourne, Dalston.

Dr. Schorlemmer delivered a lecture on the Chemistry of the Hydrocarbons.

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April 18th.

Dr. Frankland, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

Thomas Tyrer, Battersea; F. W. Fison, Christ Church, Oxford; George Blundell Longstaff, New College, Oxford; John Robins, Portsdown Road, Maida Vale; T. R. Ogalvie, Greenock; Mark Finch, Chemical Works, Victoria Docks; A. J. Dickinson, Deptford.

The following papers were read:—

"On Benzyl Isocyanate and Isocyanurate;" also "On a Compound of Sodium and Glycerin:" by Mr. E. A. Letts.

"On the Carbonic Acid in Sea Water:" by Prof. Himly.

May 2nd.

Dr. Frankland, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society :—

Richard Anderson, Riddington, Glasgow ; George Cordwent, Taunton, Somerset.

Mr. E. Riley delivered a lecture on The Manufacture of Iron and Steel.

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May 16th.

Dr. Debus, Vice-President, in the Chair.

The following gentlemen were duly elected Fellows of the Society :—

C. H. W. Biggs, Reading ; J. G. Johnson, Forest Hill ; J. A. Ormerod, Jesus College, Oxford ; Earnest H. Jacob, Corpus Christi College, Oxford.

The following papers were read :—

“ On the Influence of Pressure on Fermentation, Part I : ” by Mr. H. T. Brown.

“ On the Electrolysis of Sugar Solution : ” by Mr. H. T. Brown.

“ On the Determination of the Solubility and Specific Gravity of certain Salts of Sodium and Potassium : ” by Messrs. D. Page and A. D. Keightley.

“ An Examination of a Recent Attack upon the Atomic Theory : ” by Mr. R. W. Atkinson.

“ On the Transformation-products of Starch : ” by Mr. C. O'Sullivan.

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June 6th.

Dr. Gilbert, in the Chair.

The following gentlemen were duly elected Fellows of the Society :—

G. E. Barker, Sheffield ; H. Smith, Manchester ; R. H. Davis, Harrogate ; Richard Weaver, Leicester ; Francis Henry de Rheims, junr., Plumstead.

The following papers were read :—

“ On a Remarkable Salt deposited from the Mother-liquors obtained in the Manufacture of Soda : ” by Prof. E. T. Thorpe.



"On the Composition of Ceylon Jargons:" by Mr. M. H. Cochran.

"On a Double Sulphide of Gold and Silver:" by Mr. M. M. Pattison Muir.

"On the Solvent Action of Various Saline Solutions upon Lead:" by Mr. M. M. Pattison Muir.

"On the Magnetic Sand of Mount Etna:" by Mr. J. B. Hannay.

"New Tests for some Organic Fluids:" by Mr. J. A. Wanklyn.

"Dendritic Spots on Paper:" by Mr. A. Liversidge.

"On Chinoline and Leucoline:" by Mr. C. G. Williams.

"On some Derivatives of Chinoline:" by Mr. Dewar.

"On the Action of Phosphoric Acid on Morphine:" by Dr. Wright.

"On a Secondary Colouring Matter Produced in the Preparation of Alizarin from Anthracene:" by Mr. W. H. Perkin.

"On the Effects of Temperature on the Absorption of Gases by Charcoal:" by Mr. J. Hunter.

"On the Nitration-products of Dibromophenol-sulphonic Acids," No. V. "On Bromo-phenol-sulphonic Acid," No. VI. "On the Formation of Substituted Nitrophenol-sulphonic Acids," No. VII: by Dr. H. E. Armstrong.

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June 20th.

Dr. Frankland, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

J. Emilius Shadwell, Christ Church, Oxford; Walter Weldon, Putney; Walter Stuart, jun., Edinburgh; John Ferguson, University of Glasgow; Charles Armbruster, Shepherd's Bush; George J. Snelus, Workington; R. Wormell, Brixton.

A Lecture was delivered "On Deacon's Method of obtaining Chlorine, as illustrating some Principles of Chemical Dynamics:" by Mr. H. Deacon.

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Donations to the Library: Session 1871—1872:—

"The Royal Society's Catalogue of Scientific Papers;" Part V: from the Royal Society.

"Air and Rain; the beginning of a Chemical Climatology:" by Dr. R. Angus Smith: from the Author.

"Black's Lectures on Chemistry;" 2 vols. 4to, MSS: from John Glover, Esq.

"Supplement to Watts's Dictionary of Chemistry:" from the Author.

"A Practical Treatise on Soaps:" by Campbell Morfitt: from the Author.

"The Chemical Phenomena of Iron Smelting:" by I. Lowthian Bell: from the Author.

"The Connection of certain Phenomena with the Origin of Mineral Veins:" by J. A. Phillips: from the Author.

"On a Third Nitraniline:" by J. F. Walker and Th. Zincke: from the Authors.

"On some Points in the Chemistry of Sugar-refining:" by William Wallace, Ph.D.: from the Author.

"On Protoplasmic Life:" by F. C. Calvert, F.R.S.: from the Author.

"Report of the Committee on the Treatment and Utilisation of Sewage," re-appointed at Liverpool in 1870: from the Committee.

"The New Patent Sewage of Towns:" by J. B. Pow: from the Author.

"The Hygiene of Air and Water:" by William Procter, M.D.: from the Author.

"The Metric System:" by Mr. Stevenson, M.P.: from the Author.

"On Teaching Universities and Examining Boards:" by Dr. Lyon Playfair, C.B.: from the Author.

"Psychic Force and Modern Spiritualism:" by William Crookes, F.R.S.: from the Author.

"On Prussian Experimental Stations:" by E. Packard: from the Author.

"On the Change of Volume of Liquids under Constant Pressure:" by C. M. Guldberg: from the University of Christiania.

"On the Theory of Indefinite Combinations:" by C. M. Guldberg: from the University of Christiania.

"Report of New Chemo-Agricultural Investigations at the Agricultural College of Aas:" by A. Rosing: from the University of Christiania.

"Storm Atlas of the Norwegian Meteorological Institute:" from the University of Christiania.

"Geological Survey of the State of Ohio; with Maps and Sections:" from the Executive Department of the State.

"Address to the American Association for the Advancement of Science," August 16, 1871: by T. Sterry Hunt: from the Author.

"Circular No. 3 of the War Department, Surgeon-General's Office (U.S.); Report of Surgical Cases in the Army:" from the Department.

"Lecture on Water," delivered before the American Institute of the City of New York: from the Author.

"Cruise of the School-ship 'Mercury' in the Tropical Atlantic Ocean:" from the Department of Public Charities and Correction, New York.

"Sur un nouveau dissolvant de l'Iodure plombique:" par D. Tommasi: from the Author.

"Action de l'Iodure plombique sur quelques Acétates métalliques:" par D. Tommasi: from the Author.

"Revue de Géologie pour les Années 1868 et 1869:" par MM. Delesse et de Lapparent: from the Authors.

"Les Oscillations des Côtes de la France:" par M. Delesse: from the Author.

#### Periodicals:—

"Philosophical Transactions" for 1871: from the Royal Society.

"List of Officers and Fellows of the Royal Society for 1871:" from the Royal Society.

"Quarterly Journal of Science," 1871-72: from the Editor.

"Pharmaceutical Journal and Transactions," Third Series, Vol. II: from the Pharmaceutical Society.

"Journal of the Society of Arts," 1871-72: from the Society.

"Chemical News," 1871-72: from the Editor.

"The Chemist and Druggist," 1871-72: from the Editor.

"The Photographic Journal," 1871-72: from the Photographic Society.

"Memoirs of the Royal Astronomical Society," Vol. XXXIX: from the Society.

"Monthly Notices of the Royal Astronomical Society," 1871-72: from the Society.

"General Index to the first Thirty-eight Volumes of the Memoirs of the Royal Astronomical Society:" from the Society.

"Quarterly Journal of the Geological Society," 1871-72: from the Society.

"Nature," 1871-72: from the Editor.

"The Food Journal," 1871-72: from the Editor.

"Year-book of Pharmacy" for 1870: from the Editor.

"The British Pharmacist" for 1871: from the Editor.

"Transactions of the American Philosophical Society." New Series. Vol. XIV, Part 3: from the Society.

"The American Chemist," 1871-72: from the Editor.

"Les Mondes," 1871-72: from the Editor.

"Revue Scientifique," 1871-72: from the Editor.



"Archives Néerlandaises des Sciences exactes et Naturelles." Tome VI, Livraisons 4 et 5: from the Editor.

"Bulletin de l'Académie Impériale des Sciences de St. Petersburg," Tome XVI, Nos. 2—5: from the Academy.

"Denkschriften der Kaiserlichen Akademie der Wissenschaften (Mathematisch-naturwissenschaftliche Klasse) Band: from the Academy.

"Journal of the Iron and Steel Institute," from October, 1871, to May, 1872: from the Institute.

"Journal of the London Institution," 1871-72: from the Institution.

"Proceedings of the Literary and Philosophical Society of Manchester," 1871: from the Society.

"Annual Report of the Royal Cornwall Polytechnic Society for 1871:" from the Society.

"Transactions of the Royal Society of Edinburgh," Vol. XXVI, Parts 2 and 3: from the Society.

"Proceedings of the same," Session, 1870-71: from the Society.

"Proceedings of the Philosophical Society of Glasgow," 1870-71: from the Society.

"Journal of the Chemico-Agricultural Society of Ulster," Dec., 1871, and June, 1872: from the Society.

"American Journal of Science and Arts," from July, 1871, to June, 1872: from the Editors.

"Journal of the Franklin Institute," from June, 1871, to May, 1872: from the Institute.

"Annual Reports of the Commissioner of Patents (United States)," 1868, 4 volumes: from the Commissioner.

"Archives of Science, and Transactions of the Orleans County Society of Natural History (Vermont, United States)," April, 1871: from the Society.

"Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften zu Wien (Mathematisch-naturwissenschaftliche Klasse)," Erste Abtheilung, Band lvii, Hefte 3, 4, 5; Band lxiii, Hefte 1—5: Zweite Abtheilung, Band lxii, Hefte 4, 5; Band lxiii, Hefte 1—5; from the Academy.

"Kurze Anzeige derselben," 1871-72; from the Academy.

"Journal für praktische Chemie," 1871-72: from Prof. Kolbe.

"Berichte der deutschen chemischen Gesellschaft zu Berlin," 1871-72: from the Society.

"Zeitschrift für Chemie," siebenter Band: from the Editor.

"Verhandlungen der physikalisch-medicinischen Gesellschaft zu Erlangen," März—August, 1871: from the Society.

"Verhandlungen der physikalisch-medicinischen Gesellschaft zu Würzburg," 2ter Band, 4tes Heft: from the Society.

“Verhandlungen der naturforschenden Gesellschaft zu Basel,”  
Fünfter Theil, 1871: from the Society.

“Nieuwe Verhandelingen van het Bataafsch Genootschap der  
proefondervindelijke Wijsbegeerte te Rotterdam:” from the Society.

“Oversigt over det Kongelige Danske Videnskabernes Selskabs  
Forhandlinger, og dets Medlemmers Arbeeten,” 1871: from the  
Academy.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
BRITISH AND FOREIGN JOURNALS.

Physical Chemistry.

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On Peltier's Phenomenon and the Thermo-electric Force of  
Metals. By A. WUELLNER (Pogg. Ann., cxlv, 636).

THOMSON'S observation that the heat produced by an electric current passing through a homogeneous metallic wire which is warmer at one end than at the other, varies with the direction of the current; and Edlund's experiments, according to which the electromotive force of thermo-electric currents is not proportional to the quantities of heat generated or consumed at the points of contact, are not, as Edlund has remarked, at variance with the second law of thermodynamics: and they can easily be explained by the hypothesis of Clausius, that an unequal distribution of heat disturbs the electric equilibrium, even in a homogeneous metal, causing the electric potential either to rise or to fall from the hotter to the colder parts, according to the nature of the metal.

In an iron wire for instance, where the electric density increases from the hotter towards the colder parts, if an electric current advances from the hotter to the colder end, it will have to overcome an electromotive force which, by itself, would produce a current in the opposite direction; it will therefore generate less heat than on passing from parts of greater to parts of lesser density, in which case it would be weakened by the electromotive force due to this fall of the potential.

That the strength of the current, passing through a circuit of two metals, cannot be proportional to the quantities of heat produced or consumed at the points of contact, follows immediately from the consideration, that the total electromotive force of a thermoelectric current is equal to the algebraical sum of all the differences of the potential, reckoned in the same direction along the circuit, that is to say, equal to the electromotive force produced at the point of contact *plus* the electromotive force generated in each metal. As these forces act, according to the nature of the combination, either in the same or in opposite directions, it follows that the total current strength may increase either more or less rapidly than the difference of the temperatures at the points of contact. This is quite in accordance with the experiments of Avenarius, who finds that the electromotive force of the metallic combinations examined by him, can be expressed by the formula—

$$E = (t_2 - t_1)[a + b(t_2 + t_1)].$$

in which *b* may be either positive (zinc, copper) or negative (zinc, steel).

R. S.



**A New Arrangement of the Copper-Zinc Battery.** By J. MORIN (Compt. rend., xxiv, 1560).

THIS consists of a cylinder of copper, concentrically placed within which is a cylinder of zinc, the space between them being divided into two parts by a cylinder of filter paper. Between the paper and the copper is placed ordinary porous earthenware (grés); between the paper and the zinc, sulphur. The whole is plunged into cupric sulphate solution, which penetrates the mass through holes made in the copper cylinder.

Several hundred pairs, thus arranged, and working very frequently, lasted for 20 months without any attention, and then seemed capable of continuing to act as long again before being exhausted.

B. J. G.

**Heat of Expansion of Solids.** By H. BUFF (Pogg. Ann., cxlv, 626).

THE author has determined the actual amount of heat consumed in the expansion of solids. If, as Wertheim's researches have rendered it probable, the cubical and linear coefficients of elasticity are equal, then a cubic centimeter of iron will, on being stretched in each of its three dimensions, with a force of 160 kilograms, expand into the volume 1·0000481 c.c. The same expansion (between 0° and 100°) would be produced by an increase of temperature of 1·374° C.

The linear extension in each dimension amounting to  $\frac{0\cdot0000481}{3}$  centimeter, the total mechanical work done in the three dimensions is expressed by 160 kilograms  $\times$  0·0000481 centimeter, or 4·81 gram-centimeters.

The total heat required to raise a cubic-centimeter of iron, through 1° C. is 1·170 heat-units, which are approximately equivalent to 49140 gram-centimeters; so that the total heat absorbed is to the amount of heat spent in expansion as 49140 to 4·81, or as 10000 to ·98.

The column under  $\lambda$  in the following table shows how many of every 10,000 heat-units absorbed by a body are actually spent in its expansion:—

	$\lambda$ .		$\lambda$ .
Iron .....	·980	Platinum .....	·920
Copper .....	1·496	Lead .....	5·800
Silver .....	2·378	Glass .....	1·441
Gold .....	1·899	Water (at 16° C.)..	3·810

From the smallness of  $\lambda$  when compared with the total amount of heat absorbed by a body, it is apparent why it has not yet been found possible to raise the temperature of a solid body by compression, and why the heat rendered latent by expansion, exercises scarcely any influence upon the specific heats of the atoms of solid bodies.

R. S.

**On the Heat of Formation of the Oxygen-acids of Nitrogen.**

By JULIUS THOMSEN (Deut. Chem. Ges. Ber., v, 508).

THE author, who had determined the heat attending the reaction ( $\text{N}_2\text{O}_2, \text{O}_2, \text{Aq}$ ) by first measuring the heat due to ( $\text{N}_2\text{O}_2, \text{O}_2$ ), and then that due to ( $\text{N}_2\text{O}_4, \text{Aq}$ ), meets Berthelot's objection, that perhaps the first of these reactions was completed only after contact with water, by the remark that for the total heat of the reaction ( $\text{N}_2\text{O}_2, \text{O}_2, \text{Aq}$ ) it is quite immaterial whether the nitrogen tetroxide is completely formed or not before the gases which produce it come into contact with water.

Berthelot's suggestion, that the reaction ( $\text{NO}, \text{O}$ ) was slow and gradual, is not borne out by the author's experiments, who found his results to be independent of the time during which the gases remained in the calorimeter.

The author considers it impossible that the reaction ( $\text{N}_2\text{O}_4, \text{Aq}, \text{O}$ ) which he effected by chlorine could, as Berthelot supposes, in any way be due to the presence of aqua regia, the formation of which in a solution containing only 1 molecule of  $\text{N}_2\text{O}_4$  in 733 molecules of water is out of question.

As besides, the numbers obtained by oxidation with chlorine were confirmed by those obtained by oxidation with potassium permanganate, the author thinks himself justified in considering his determination ( $\text{N}_2\text{O}_2, \text{O}_3, \text{Aq}$ ) = ( $\text{N}_2\text{O}_2, \text{O}_2, \text{Aq}$ ) + ( $\text{N}_2\text{O}_4, \text{Aq}, \text{O}$ ) = 72941 heat units, as trustworthy, and independent of any hypothesis.

R. S.

**The Freezing of Saline Solutions.** By FR. RÜDORFF (Pogg. Ann., cxlv, 599).

THE first part of the paper being partly an answer to M. de Coppet's objections to some of the author's results concerning the freezing of saline solutions, contains the several reasons, which render it probable that only ice and no salt separates from weak solutions, the following fact being considered decisive. A fragment of ice, thrown into a solution of sodium sulphate, causes solidification of water only, whilst by contact with a crystal of sodium sulphate, the crystallisation of the salt only is provoked; if, on the other hand, pieces of ice, and of the crystallised salt, are thrown in simultaneously, water and salt solidify at the same time. From this the author infers, that if in the first case, a mere trace of salt had separated along with the ice, the whole quantity of salt in the solution would have been caused to solidify, &c. Besides, supposing that ice containing particles of salt had been deposited, then the salt in contact with the ice could not remain solid, but would, as in the case of freezing mixtures, dissolve again; but it is improbable that crystals of the salt should be formed under circumstances under which they cannot exist.

Numerous experimental data are then given, proving that the value of  $\frac{T}{M}$ , where M denotes the quantity of salt dissolved in 100 parts of water, and T the temperature of the solution, remains constant for most salts, and that in those cases where T and M do not increase in the same

ratio, this irregularity may be made to disappear by a certain assumption about the state of hydration in which the salt is present in the water. For instance, in the case of ammonio-manganous sulphate  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{MnSO}_4 + 6\text{H}_2\text{O}$ , and of ammonium-cadmium sulphate  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CdSO}_4 + 6\text{H}_2\text{O}$ ,  $T$  increases more slowly than  $M$  if  $M$  is calculated as the hydrate; but they increase in the same ratio if  $M$  represents the quantity of anhydrous salt dissolved in 100 parts of water.

Other salts must be supposed to be dissolved as hydrates, and some hydrates appear on dissolving to change their state of hydration. A formula is given, from which the number of molecules of water with which they then combine, can be calculated if the freezing points of two solutions of the salts of different strengths are determined.

In the case of some salts, as silver nitrate, and acetic hydrate, no satisfactory explanation could be given of the irregularity of the quotient,  $\frac{T}{M}$ .

The state of hydration of barium chloride, as in the case of the chlorides of sodium and of copper, seems to depend upon the temperature and the degree of concentration, inasmuch as it appears to be dissolved, as  $\text{BaCl}_2 + 2\text{H}_2\text{O}$ , in solutions containing less than 24 parts of the (anhydrous) salt, and as  $\text{BaCl}_2 + 6\text{H}_2\text{O}$  in stronger solutions.

The following formulæ express, according to the author, the constitution of several salts when in solution:—

$(\text{NH}_4)_2\text{O} + 2\text{H}_2\text{O}$ ;  $\text{K}_2\text{O} + 5\text{H}_2\text{O}$ ;  $\text{Na}_2\text{O} + 4\text{H}_2\text{O}$ ;  $\text{HCl} + 6\text{H}_2\text{O}$ ;  $\text{NaCl}$ ;  $\text{NaCl} + 2\text{H}_2\text{O}$ ;  $\text{KCl}$ ;  $\text{NH}_4\text{Cl}$ ;  $\text{CaCl}_2 + 6\text{H}_2\text{O}$ ;  $\text{BaCl}_2 + 2\text{H}_2\text{O}$  and  $\text{BaCl}_2 + 12\text{H}_2\text{O}$ ;  $\text{SrCl}_2 + 12\text{H}_2\text{O}$ ;  $\text{MnCl}_2 + 12\text{H}_2\text{O}$ ;  $\text{CoCl}_2 + 12\text{H}_2\text{O}$ ;  $\text{NiCl}_2 + 12\text{H}_2\text{O}$ ;  $\text{CuCl}_2 + 4\text{H}_2\text{O}$ ;  $\text{CuCl}_2 + 12\text{H}_2\text{O}$ ;  $\text{CuCl}_2 \cdot 2\text{NH}_4\text{Cl} + 4\text{H}_2\text{O}$ ;  $\text{HI} + 4\text{H}_2\text{O}$ ;  $\text{KI}$ ;  $\text{NaI} + 4\text{H}_2\text{O}$ ;  $\text{CdI}_2 + 12\text{H}_2\text{O}$ ;  $\text{KBr}$ ;  $\text{NaBr} + 4\text{H}_2\text{O}$ ;  $\text{H}_2\text{N}_2\text{O}_6 + 9\text{H}_2\text{O}$ ;  $\text{CaN}_2\text{O}_6 + 12\text{H}_2\text{O}$ ;  $\text{MnN}_2\text{O}_6 + 12\text{H}_2\text{O}$ ;  $\text{CdN}_2\text{O}_6 + 12\text{H}_2\text{O}$ ;  $\text{NiN}_2\text{O}_6 + 12\text{H}_2\text{O}$ ;  $\text{H}_2\text{SO}_4 + 9\text{H}_2\text{O}$ ;  $\text{K}_2\text{SO}_4$ ;  $\text{Na}_2\text{SO}_4$ ;  $(\text{NH}_4)_2\text{SO}_4$ ;  $\text{MgSO}_4 + 7\text{H}_2\text{O}$ ;  $\text{ZnSO}_4 + 7\text{H}_2\text{O}$ ;  $\text{NiSO}_4 + 7\text{H}_2\text{O}$ ;  $\text{CuSO}_4 + 5\text{H}_2\text{O}$ ;  $\text{MnSO}_4 + 12\text{H}_2\text{O}$ ;  $\text{MnSO}_4(\text{NH}_4)_2\text{SO}_4$ ;  $\text{CdSO}_4(\text{NH}_4)_2\text{SO}_4$ ;  $\text{K}_2\text{CrO}_4$ ;  $\text{NaC}_2\text{H}_3\text{O}_2 + 5\text{H}_2\text{O}$ ;  $\text{K}_2\text{CO}_3$ ;  $\text{KCNS}$ .

R. S.

### On the Simplest Method of ascertaining the Molecular Weight by the Vapour-volume. By R. LANDOLT (Deut. Chem. Ges. Ber., v, 497).

To ascertain the molecular vapour-volume of a liquid, the author introduces the molecular weight in milligrams of a well-defined substance—for instance, 18 milligrams of water or 119.5 milligrams of chloroform—into one of two glass tubes of equal length (750 mm.) and diameter, filled with and standing over mercury, and brings the supposed molecular weight in milligrams of the substance to be examined, into the other tube. Now, when steam, or the vapour of a liquid less volatile than water is admitted into the glass cylinder surrounding both tubes, the mercury in them will be at the same level, if the assumed molecular weight was the right one, whilst a difference in the level indicates at once whether too great or too small a molecular weight was ascribed to the substance.



The same principle is applied to demonstrate by an easy lecture experiment, that the molecules of different bodies in the gaseous state occupy equal volumes.

R. S.

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**The Laws which Regulate the Distribution of a Substance between Two Solvents.** By BERTHELOT and JUNGFLEISCH (Ann. Chim. Phys. [4], xxvi, 396—417).

ALTHOUGH chemists frequently resort to the purely physical process of extracting a substance dissolved in one liquid, by agitating it with another liquid not miscible with the first, the laws which govern this molecular action have not hitherto been studied.

The present essay consists of three parts. 1. Experiments on the distribution of a substance between two solvents, made in conjunction with Jungfleisch. 2. Theory of this distribution. 3. Experiments on the state of dissolved salts, made with L. de Saint-Martin.

The authors have studied the solubility of iodine and bromine in water and carbon disulphide, also of succinic, malic, tartaric, oxalic, acetic, benzoic, sulphuric, and hydrochloric acids and ammonia in water, and in ether. The method of experimenting was to dissolve the substance in one of the liquids, and then agitate it with a known volume of the other, the amount of substance being determined in each of the superposed liquids when they had become saturated.

It is found that when a substance is simultaneously in presence of two solvents, the quantities dissolved by equal volumes of the two liquids have a constant ratio, which is called the *coefficient of distribution*, and is independent of the relative volumes of the two solvents, but varies with the degree of concentration, and with the temperature. In the case of succinic acid, a decrease of temperature causes a diminution of the coefficient of distribution, and the same effect is produced by dilution. With oxalic, malic, tartaric, and acetic acids, on the contrary, the coefficient increases with the dilution, and the same with ammonia. The coefficient for iodine with water and carbon disulphide, may be regarded as independent of the degree of concentration.

The fact, that the coefficient of distribution is independent of the relative volume of the two solvents, may be readily explained in the following manner:—Imagine the superposed liquids to be saturated with the substance: then for equilibrium to persist, it is only necessary that there should be equilibrium at the surface of contact of the two liquids, and this would be undisturbed by the addition of an arbitrary volume of the same liquid saturated to the same degree, to either of the superposed liquids. From the consideration of the influence of concentration, it is evident that as the solutions become more dilute, the coefficient of distribution approaches a certain limit, so that if it is desired to remove a substance from a solution by agitating it with another liquid, it is advisable to employ the latter in successive fractions (*ib.* [4], xx, 422—425). Moreover, it is easy, by successive determinations of the coefficients of distribution, to ascertain whether the substance dissolved is homogeneous or a mixture (*ib.* [4], xx, 425, 429, and 431). As there is a limit to the coefficient as the solutions

become more dilute, there will likewise be one as they become more concentrated, and it would naturally be supposed that this limit would be the ratio of the two liquids when saturated separately; but experimentally this has been found not to be the case, the coefficient being less than that corresponding to the ratio of the solubilities. With respect to the relation between the coefficient of distribution and the chemical composition of the substance dissolved, the authors find that ether removes more readily from their aqueous solutions: 1. The more highly carburetted of two homologous acids. 2. The monobasic rather than the corresponding bibasic acid (*e.g.*, butyric than succinic acid). 3. Or than the bibasic acid having nearly the same percentage composition (acetic acid and succinic acid); also (4) of acids containing the same carbon and hydrogen, that which has least oxygen (succinic and malic acids).

In the case of two substances in presence of two solvents, they are distributed as if each of the substances acted alone. This relation is analogous to the law of the solubility of mixed gases, and is capable of being applied to the separation of two mixed substances (*ib.* [4], xx, 425—431).

C. E. G.

**A Relation between the Surface-tension of Liquids and the Supersaturation of Saline Solutions.** By CHARLES TOMLINSON and G. VAN DER MENSTRUGGHE (Proc. Roy. Soc., xx, 342; Chem. News, xxv, 281, 297).

THE authors refer to former researches, from which, taken along with experiments described in the present paper, they conclude:—

1. That a supersaturated saline solution in a chemically clean flask, will remain liquid so long as its free surface, or the surface in contact with the sides of the flask, does not undergo in one or many points a notable diminution of surface-tension.

2. That in such a solution, a drop of a liquid of feeble tension produces crystallisation.

3. That a liquid of comparatively high surface-tension, which does not act chemically on the solution, may remain in contact with it for some time without any crystallisation ensuing.

4. A solid covered with a film of a liquid of feeble tension produces change of state.

The application of heat proved insufficient to lower the tension of supersaturated solutions so as to induce crystallisation.

Vapours of alcohol, chloroform, &c., were also insufficient to produce this action.

The results of a few experiments did not coincide with the expectations deduced from proposition (2). The observation of Quincke that such exceptional results may be explained by supposing the presence of an impurity in the form of a film on the liquid experimented with, is not generally to be allowed as satisfactory. The weather, according to the authors, exercises a powerful action in lowering or increasing the tension of the liquids; the viscosity of the liquid surfaces, also, must be taken into account.

M. M. P. M.

**Convenient Apparatus for Evolving Gases.** By V. WARTHA  
(Deut. Chem. Ges. Ber., v, 561—563).

A VERY convenient apparatus for evolving a small quantity of hydrogen sulphide at a time, may be constructed with a flask arranged like a wash-bottle, the shorter tube being provided with a Mohr's clamp. By blowing into it, the acid is forced into the wider tube, which is drawn out into a point and filled with small pieces of glass and ferrous sulphide, resting on a perforated caoutchouc-plate. By opening the clamp the evolution of gas is stopped at once.

An apparatus on a larger scale is also described, but it cannot well be understood without a figure.

C. S.

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## Inorganic Chemistry.

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**Absorption of Ozone by Water.** By L. CARIUS (Deut. Chem. Ges. Ber., v, 520—526).

THE solubility of ozone in water has been affirmed by some and denied by other chemists. The author's experiments prove that water does absorb considerable quantities of ozone at low temperatures.

The absorption-coefficient of ozone in water cannot be properly determined, but the author gives the amounts of ozone absorbed under certain pressures and at given temperatures.

The ozone was prepared by Soret's method (electrolysis of cold dilute sulphuric acid, platinum-iridium wires being used as electrodes). The gas, mixed with oxygen, being passed through water, the amount of ozone absorbed was determined by estimating the quantity of iodine liberated from a potassium iodide solution with which the ozone-water had been shaken up.

1000 c.c. distilled water absorbed—

- |     |      |  |
|-----|------|--|
| (1) | 5.11 | c.c. ozone at 0° and 0 mm. .76 pressure. |
| (2) | 4.24 | "      "      "      "      "            |
| (3) | 3.86 | "      "      "      "      "            |

Commercial ozone water obtained from a Berlin firm, contained per 1000 c.c. at 0° and .76 mm. pressure—

- |     |      |            |
|-----|------|------------|
| (1) | 4.45 | c.c. ozone |
| (2) | 4.06 | "      "   |

The absorption of gas by water is, therefore, very considerable, the pressure at which these experiments were conducted being so very small.

M. M. P. M.



**Contribution to the Chemistry of Atmospheric Deposits; Amounts of Nitrates in Spring, Brook, River, and Lake-water.** By F. GOPPELSROEDER (*Zeitschr. Anal. Chem.*, xi, 16).

THIS paper gives the results of a large number of nitric-acid determinations in Swiss and Baden waters, being a continuation of the author's work on the above subject (this Journal, 1871, p. 324).

A. T.

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**Reduction of Sulphuric Acid to Hydrogen Sulphide by Hydrogen in the Nascent State.** By H. KOLBE (*Dingl. Polyt. J.*, cciv, 160).

IT is universally known that sulphurous acid is reduced to sulphur and hydrogen-sulphide by hydrogen in the nascent state, liberated by the reaction of zinc and sulphuric or hydrochloric acid. It does not appear, however, to be generally known, that a similar reduction takes place in the case of sulphuric acid. During several years the author has observed repeatedly that hydrogen prepared by the action of zinc and sulphuric acid, possesses strongly the odour of hydrogen sulphide, and blackens lead paper. It was at first thought that the sulphuric acid contained sulphurous acid, but subsequently it was found that chemically pure sulphuric acid yielded hydrogen sulphide in quite as large quantity as the commercial acid. This gas was obtained more abundantly, the hotter the acid liquid, and the more concentrated the sulphuric acid which comes in contact with the zinc. If the sulphuric acid be previously diluted with about double its volume of water, the escaping hydrogen is absolutely free from hydrogen sulphide.

The author adverts to the importance of obtaining a stream of hydrogen perfectly free from sulphur, in detecting the presence of small quantities of arsenic by the Marsh's apparatus, as without this precaution the arsenic may be converted into sulphide, and so escape detection; it is absolutely necessary, therefore, for this purpose, to use dilute sulphuric acid.

W. S.

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**Crystallised Phosphoric Acid.** By EMIL ZETTNOW (*Pogg. Ann.*, cxlv, 643).

ON some sticks of glacial phosphoric acid, which had been kept for more than a year in bottle, with a badly fitting stopper, and in the mother-liquor at the bottom, some shining crystals were observed, which, after having been freed from the adhering liquid by pressure between bibulous paper, gave, immediately after solution in water, all the reactions characteristic of ordinary phosphoric acid; they contained no metal, except a trace of sodium, recognisable only by the coloration which they imparted to a flame. The numbers obtained by fusion

with lead oxide, as well as the determination of the water, correspond however with the formula  $P_2O_5 \cdot 2H_2O$ , from which it appears probable that the crystals consist of pyrophosphoric acid, which on dissolving in water, instantly change into the tribasic acid.

R. S.

**Hypophosphites.** By C. RAMMELSBURG (Deut. Chem. Ges. Ber. [2], v, 492—497).

THE author has re-examined the effects of heat upon the hypophosphites, and has added to the number of these salts previously known, those of lithium, thallium cerium and uranium.

The thallium, cadmium, calcium and lead-salts have no water of crystallisation; the others lose theirs between  $100^\circ$ — $200^\circ$  without decomposition, except that the nickel and cobalt salts cannot be heated above  $130^\circ$ — $140^\circ$  without undergoing change. The lithium and barium salts crystallise with one molecule of water, their crystals and those of the calcium and lead salts belonging to the monoclinic system: the magnesium, zinc, nickel and cobalt salts crystallise with six molecules of water, their crystals belonging to the regular system.

According to H. Rose, most of the hypophosphites are converted by heat into (pyro) phosphates, water, and hydrogen phosphide, half the phosphorus becoming gaseous; the dark residues nearly insoluble in acids left by the nickel and cobalt salts are what we should now describe as pyrophosphate and metaphosphate; and cadmium hypophosphite yields a residue consisting, in modern nomenclature, of one molecule of pyrophosphate to one of metaphosphate. These conclusions prove to be incorrect: with regard to that concerning the residue from the cadmium salt, inspection of its formula is sufficient to show that it does not contain a proportion of oxygen large enough to enable it to behave as stated.

When the hypophosphites are heated, the residues never consist exclusively of pyrophosphate, but in most cases of this salt mixed with metaphosphate. Those from the nickel and cobalt salts are mixtures of metaphosphate and phosphide, and consequently increase in weight when oxidised by nitric acid. The ratio of pyrophosphate to metaphosphate in the residue varies: in those from the sodium, thallium and lithium salts it is 1 : 1 molecule, and as the ratio of oxygen to metal in these mixtures is the same as in the original salts, no water is given off during the decomposition; in those from the magnesium, zinc, and manganese salts, it is 2 : 1; in those from the strontium, calcium, cerium and cadmium salts it is 3 : 1; in that from the lead salt it is 4 : 1; and in that from the barium salt, the examination of which led Rose to the conclusion he arrived at, almost unavoidably in the absence of any known method of satisfactorily estimating phosphoric acid, it is 6 : 1, there being only 13 atoms of barium to 14 of phosphorus, instead of an equal number, as Rose believed. Ammonia hypophosphite leaves a residue of one molecule of pyrophosphate to two of metaphosphate. Uranium hypophosphite, which is the hypophosphite

of uranyl, is converted into phosphate with incandescence and explosive violence, the residue consisting of three molecules of uranous pyrophosphate, one of uranous metaphosphate, and one of uranium phosphide,  $U_2P$ , while hydrogen alone escapes.

It is evident, therefore, that the ratio of the phosphorus which remains fixed to that which becomes gaseous varies, but is never that of 1 : 1, as it has so long been supposed to be.

The author has already shown (*Pogg. Ann.* cxx, cxxxi) that when phosphites are heated, they leave either pyrophosphate or a mixture of this with phosphide, and give off only hydrogen, none of the phosphorus escaping and no water being formed. Uranium hypophosphite agrees, therefore, with the phosphites in its behaviour when heated.

E. D.

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### The Solubility of Calcium Carbonate in Carbonic Acid Water.

By T. SCHLÖSING (*Compt. rend.*, xxiv, 1552—1556).

THE author, being engaged in investigating the solutions contained in soils, found it necessary to prepare a variety of similar solutions made under different and well-defined conditions. In this paper he gives the results of his experiments on the solubility of calcium carbonate in water, into which different mixtures of air and carbon dioxide were passed, the temperature remaining constant. By hydraulic arrangements he produced two streams of purified air and carbon dioxide, whose velocity could be maintained unaltered for any length of time. These streams were mixed before entering the vessel containing calcium carbonate\* and water, and a solvent of constant composition for each experiment was thus ensured. After the gas had passed for about a week, each solution was siphoned through a filter placed under a bell-jar containing an atmosphere of the same composition and temperature as that passed into the liquid to be filtered. The filtrate was collected in an exhausted weighed balloon-receiver, and, after its weight had been ascertained, was boiled with acid, and the evolved carbon dioxide estimated, the lime being determined with ammonium oxalate. The results of 12 experiments are given in the following table for 1 litre of water at 16°. The pressures given are calculated from the known composition of the various gaseous mixtures used, and refer to the carbon dioxide only; the numbers under this head are fractions of 760 mm. taken as unity:—

\* The physical condition and source of the calcium carbonate is not stated.



Experiment.	Pressures.	Carbon dioxide.	Calcium carbonate.
		mgms.	mgms.
I.....	0·000504	60·96	74·60
II.....	0·000808	72·11	85·00
III.....	0·00333	123·00	137·20
IV.....	0·01387	218·36	223·10
V.....	0·0282	310·40	296·50
VI.....	0·05008	408·50	360·00
VII.....	0·1422	?	533·00
VIII.....	0·2538	1072·2	663·40
IX.....	0·4167	1500·5	787·50
X.....	0·5533	1846·3	885·50
XI.....	0·7297	2269·8	972·00
XII.....	0·9841	2864·2	1086·00

The gas used in Experiment I contained the proportion of carbon dioxide present in atmospheric air; that in Experiment XII was pure carbon dioxide.

The solubility of carbon dioxide and of calcium carbonate in pure water at 16° (pressure not stated) was then determined, and found to be, for 1 litre:—

Calcium carbonate..... 13·1 milligrams.  
Carbon dioxide ..... 1948·3 „

The author thinks that the presence of an acid carbonate would not sensibly affect the power of water to dissolve carbon dioxide according to the law of absorption, and calcium carbonate to the same extent as in pure water, and calculations made on the basis of the above results seem to confirm this theory:—

Taking, *e.g.*, Experiment VI, we find:—

Total carbonate found for 1 litre.....	mgms. 360·0
Neutral carbonate dissolved by 1 litre pure water	13·1
Carbonate corresponding to the bicarbonate ....	346·9
CO <sub>2</sub> of the neutral carbonate .....	5·76
„ „ bicarbonate .....	305·30
„ (free) according to law of absorption .....	97·57
Total .....	408·63
Found.....	408·50

The relation of the calculated to the experimental numbers will be found to be very close in all the other cases also.

The author concludes (1.) That in presence of calcium carbonate and of an excess of an atmosphere containing a constant proportion of carbon dioxide, water dissolves free carbon dioxide, neutral carbonate, and bicarbonate. (2.) That the solution of the carbon dioxide takes place just as in pure water in accordance with the law of absorption. (3.) That the solution of the neutral carbonate takes place just as in pure water. (4.) That the solution of the bicarbonate depends for a

given temperature on the tension of the carbon dioxide contained in the atmosphere employed.

Assuming the atmosphere contained in soils devoted to agriculture to have on an average 1 per cent. of carbon dioxide (Boussingault and Lewy), a litre of water in such soils should contain about 110 mgms. calcium oxide combined with carbon dioxide.

B. J. G.

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**Silver Fluoride.** By G. GORE (Proc. Roy. Soc., xxx, 70; Chem. News, xxiv, 291).

THE action of iodine and heat on silver fluoride produces iodine fluoride and silver iodide, also, if the temperature approaches redness, corroding the platinum vessels and forming a double salt of silver iodide and platinum fluoride. Iodine fluoride is a volatile colourless fuming liquid, which by itself does not corrode mercury or red-hot platinum, but corrodes glass at 15°, and silicon crystals at a red heat. It blackens a deal splint, and is decomposed by water into hydrofluoric and iodic acids.

Silver fluoride is reduced by heating in dry cyanogen vapour, or hydrogen cyanide, or coal gas, but is unaffected by carbon oxide or dioxide, silicon fluoride, sulphur dioxide, or sulphur fluoride vapour, or by liquid cyanogen, carbon disulphide, hydrogen cyanide (dry), carbon tetra- or trichloride, pure carbon, or boron crystals. Fused in the vapour of carbon tri- or tetrachloride, it forms silver chloride, as well as an insoluble double salt of silver and platinum by corrosion of the vessels. A solution of bromine or iodine in carbon tetrachloride or disulphide is quickly decolorised by agitation with silver fluoride. It is also decomposed violently by fusion with vitreous boric acid, silicon, dry silica, or sulphur. In the latter case sulphur fluoride, a heavy colourless gas of a peculiar dusty odour, is evolved. Sulphur chloride with silver fluoride either fused or in solution, gives silver chloride and sulphide. Carbon disulphide vapour at a red heat yields silver sulphide and carbon tetrafluoride.

C. G. S.

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**New Process for Preparing Platinum Black.** By J. LAWRENCE SMITH (Dingl. Polyt. J., cciv, 76).

POTASSIUM platino-chloride is used for this purpose. It is placed in a porcelain or platinum dish, and covered with a circular plate which fits inside the dish, and has an aperture in the centre to receive the tube from a hydrogen apparatus. Hydrogen gas is passed over it, and the dish is heated by an arrangement which keeps the temperature within the limits of 225°—260°. If the temperature rises too high, the platinum-black is not obtained in so good a condition. After the potassium chloride is well washed out, the product is further washed with a solution of aqueous potash or soda, and lastly with distilled water, and dried at a temperature not exceeding 105°.

W. S.

**A New Series of Platinum Compounds.** By P. SCHÜTZENBERGER  
(Bull. Soc. Chim. de Paris [2], xvii, 482—496).

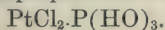
*Phosphoplatinous Chloride*.—Spongy metallic platinum is readily attacked at 200° by phosphorus pentachloride, and a well-defined compound, crystallising in beautiful reddish-yellow crystals is formed. The formula,  $\text{PtCl}_2.\text{PCl}_3$ , represents its composition.

*Phosphoplatinic Chloride*.—The compound  $\text{PtCl}_2.\text{PCl}_3$ , unites directly with another molecule of phosphorus trichloride, to form in a similar manner a lemon-yellow crystalline compound; the formula for which is  $\text{PtCl}_2.2\text{PCl}_3$ .

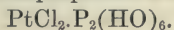
These two compounds form the starting points of a long and interesting series of derivatives.

When treated with water, both the foregoing compounds exchange the chlorine of the phosphorous chloride for hydroxyl, and form polybasic acids, thus—

Phosphoplatinous acid.



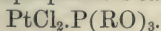
Phosphoplatinic acid.



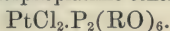
Phosphoplatinic chloride when acted upon by warm water, loses an extra atom of hydrochloric acid, leaving the compound  $\text{P}_2(\text{HO})_6\text{O}$ ,  $\text{PtCl}$ .

The two chlorides when treated with an alcohol, eliminate hydrochloric acid, and form the corresponding ether—

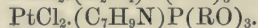
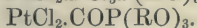
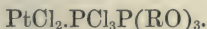
Phosphoplatinous ether.



Phosphoplatinic ether.

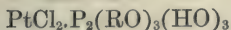


The ethers of the first series, as well as phosphoplatinous chloride, unite directly with phosphorus trichloride, carbonic oxide, ethylene, and with the aromatic compound ammonias. Bodies may thus be prepared, as represented by the following formulæ:—



The combination  $\text{PtCl}_2.\text{PCl}_3\text{P}(\text{RO})_3$  reacts with water and the alcohols, forming acid ethers and mixed ethers:

Acid ether.



Mixed ether.



Glycerin also reacts upon the phosphoplatinous and phosphoplatinic chlorides, disengaging hydrochloric acid; it has, however, been found impossible to separate the resulting products from the excess of glycerin necessarily employed.

The study of the very numerous combinations of ammonia with the phosphoplatinum compounds is incomplete; they are, therefore, but briefly mentioned in the present paper. The compounds of ammonia with the phosphoplatinum ethers, as far as they are known, appear to have the composition represented by the formulæ—



## Platinous.

1.  $P(RO)_3PtN_2H_4.2HCl$
2.  $P(RO)_3NH_3PtN_2H_4.2HCl$ .

## Platinic.

3.  $P_2(RO)_6PtN_2H_4.2HCl$ .

The ammoniacal derivatives Nos. 2 and 3, easily lose one-half of their chlorine as chloride of the alcohol-radical, and at the same time disengage ammonia. No. 1 also decomposes and loses half of its chlorine in a similar manner, but the resulting compound  $P(RO)_2ONH_3PtNH_2.2HCl$  is stable. The phosphoplatinum ethers, when treated with silver nitrate, exchange their chlorine for the nitric residue of the silver salt, thus:  $P(RO)_3PtN_2O_6$ ; and phosphoplatinic acid treated in a similar manner, exchanges not only its chlorine against the residue  $NO_3$ , but also the hydrogen of its hydroxyls for silver. It does not, however, seem possible to remove the whole of the chlorine in this way.

For details relating to the preparation of the foregoing substances, we must refer the reader to the original paper, in which will be found also the special methods adopted for the analysis of these complex compounds of phosphorus and platinum. The following are some of the analytical results:—

Phosphoplatinous chloride melts at about  $170^\circ$ . It is soluble in carbon tetrachloride, chloroform, benzene, and toluene, and may be readily crystallised from these solvents. When carefully heated it splits into phosphorus trichloride and platinous chloride, but if the heat be suddenly applied, it gives off phosphorus pentachloride, and leaves a residue of platinum.

Analysis of the air-dried crystals gave—

	Pt.	P.	Cl <sub>5</sub> .
Theory .....	48.5	7.6	43.7 = 99.8
Experiment .....	48.46	7.45	43.56 = 99.47

Phosphoplatinic chloride melts at  $160^\circ$ . It is soluble in the same liquids as the platinous compound, and decomposes in a similar manner when heated.

Analysis:—

	Pt.	P <sub>2</sub> .	Cl <sub>5</sub> .
Theory .....	36.28	11.42	52.30 = 100.0
Experiment .....	36.47	11.38	52.29 = 100.14

The decomposition of this latter chloride with water above  $12^\circ$  was ascertained by fractional precipitation with silver nitrate. In this way it was shown that the compound,  $P_2O(HO)_5PtCl$ , is first produced; that this body next exchanges half of its chlorine for  $NO_3$  (which necessitates a duplication of the formula), and that the complex acid so produced reacts still further with silver nitrate to form a silver salt, containing at the same time both chlorine and nitric acid.

Phosphoplatinous acid crystallises in prismatic, orange-yellow, deliquescent crystals, which upon analysis gave results accurately coinciding with the formula before mentioned. An attempt to prepare a definite silver salt was not very successful, inasmuch as a mixture of several salts always resulted; however, the existence of the compound,

$\text{PtCl}_2 \cdot \text{P}(\text{AgO})_2(\text{HO})$ , was satisfactorily made out. A lead salt,  $\text{P}_2\text{Pb}_3\text{O}_6\text{Pt}_2\text{Cl}_4 \cdot 2(\text{PbO}) + 4\text{H}_2\text{O}$ , was also prepared.

It is right to mention that Baudrimont was the first to notice the reaction between platinum and phosphorus pentachloride, but he interpreted the results in a different manner, and did not carry out the investigation to the extent that Schützenberger has done.

J. W.

## Mineralogical Chemistry.

**Amblygonite and Montebbrasite.** By DESCLOIZEAUX (Compt. rend., lxxiii, 1247—1258; lxxv, 114). PISANI (*ibid.*, lxxv, 79).

THE lithio-aluminic fluo-phosphates found at Penig in Saxony, and at Hebron in the State of Maine (U.S.), have hitherto been regarded as identical, and designated as *amblygonite*. In the course of last year a mineral of similar composition, but supposed to differ from *amblygonite* in the relative proportions of its constituent elements, and in its optical properties, was found in the stanniferous strata of Montebbras (Creuse), and was named *montebbrasite* (p. 892 of last volume). Subsequently this mineral was analysed by Pisani, v. Kobell, and Rammelsberg (pp. 126, 468 of this volume), who concluded that it was identical in composition with the *amblygonite* of Saxony; that from Hebron had not then been analysed. More recently, however, Pisani has analysed the American mineral, and finds that it is a hydrated fluo-phosphate of aluminium and lithium not containing sodium, whereas the Saxon mineral is an anhydrous phosphate of aluminium, lithium, and sodium; and Descloizeaux has shown that the two minerals differ in their optical properties. Further, it is now known that both these minerals occur in the stanniferous strata of Montebbras, though in very different quantities, the more abundant being identical with the sodio-lithio-aluminic fluophosphate of Penig, the less abundant with the lithio-aluminic fluophosphate of Hebron; and it is proposed by Descloizeaux and Pisani to designate the former by the old name of *amblygonite*, the latter by that of *montebbrasite*.

Both minerals are triclinic. *Amblygonite* occurs in laminar masses, opaque, or more or less translucent, and having a dull-white or faint-violet colour. It cleaves imperfectly, but with about equal facility, in two directions, inclined at an angle of about  $105^\circ 44'$ ; the reflected images from the two cleavage-surfaces differ slightly in brightness, but not nearly so much as those of the *montebbrasite* of Hebron. It melts easily in the flame of a spirit-lamp, without decrepitation, but with slight tumefaction, to a white opaline glass. To the blow-pipe flame it imparts a reddish-yellow colour, due to the occurrence of sodium and lithium in about equal proportions. The optical properties of the *amblygonite* of Montebbras agree exactly with those of the Saxon mineral.

*Montebbrasite* occurs at Montebbras, in small quantity, in greenish-white laminar masses, much more transparent than *amblygonite*; at Hebron also in laminar masses and in distinct four-sided prisms. It

cleaves in three directions inclined to one another at angles of  $135^\circ$ ,  $105^\circ$ , and  $88^\circ 30'$  (Descloizeaux, *Compt. rend.*, lvii, 357); sp. gr. 3.010 for the Montebbras mineral; 3.029 for that of Hebron. It melts before the blowpipe to a white enamel, and colours the flame a fine red, without any yellow tinge. In the spectroscope it exhibits the lithium line. Heated in a tube, it decrepitates more or less strongly (especially that of Montebbras), giving off water which has an acid reaction and corrodes the glass strongly (Pisani).

The difference of chemical composition of amblygonite and Montebbrasite is shown by the following analyses:—

	Amblygonite		Montebbrasite	
	from Penig. Rammelsberg.	from Montebbras. Pisani.	from Montebbras. Pisani.	from Hebron. Pisani.
F.....	8.11	8.20	3.80	5.22
P <sub>2</sub> O <sub>5</sub> ....	47.58	46.15	47.15	46.65
Al <sub>2</sub> O <sub>3</sub> ....	36.88	36.32	36.90	36.00
MnO ....	—	0.40	—	—
Li <sub>2</sub> O ....	6.68	8.10	9.84	9.75
Na <sub>2</sub> O ....	3.29	2.58	—	—
K <sub>2</sub> O ....	0.43	—	—	—
H <sub>2</sub> O ....	—	1.10	4.75	4.20
	102.97	102.85	102.44	101.82

*Wavellite of Montebbras.*—This wavellite has been found associated with amblygonite, on which it forms coatings or rather thick crusts. It exhibits the ordinary characters of wavellite, and when heated in a tube, gives off water which has an acid reaction and attacks the glass. It dissolves in sulphuric acid with evolution of hydrofluoric acid, and easily in caustic potash. Sp. gr. 2.33. Gives by analysis 34.30 p. c. P<sub>2</sub>O<sub>5</sub>, 38.25 Al<sub>2</sub>O<sub>3</sub>, 26.60 water, and 2.27 fluorine (Pisani).

H. W.

**Calcium Borate from Tarapaca, Peru.** By THIERCELIN (*Bull. Soc. Chim. de Paris* [2], xvii, 387—390).

THE mineral is collected in the dried-up bed of a river on the Pampa of Tamarugal, by digging out the sand underneath the surface-crust of salt. It is found in white nodules, having a shining, pearly, lamellar fracture, associated with yellowish prisms of glauberite, the whole being almost completely soluble in strong acids, but very slightly in water. It originates probably from the acid emanations of the neighbouring volcano of Isluga, combined with the calcium carbonate of the soil. In composition it is a calcium diborate with 8 molecules of water, and with varying quantities of glauberite, sodium chloride, silica, alumina, and iron. The boric acid averages 17 per cent.

The analysis is effected by adding standard dilute hydrochloric acid to the finely-powdered mineral suspended in water coloured blue with litmus. As soon as all the borate has been decomposed, the litmus is reddened; the amount of acid used indicates the proportion of boric acid in the substance.

C. G. S.



**Beryl from Elba.** By E. BECHI (Jahrbuch für Mineralogie, 1872, 95).

THE specimen examined had a specific gravity of 2·699—2·710, and the following composition :—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Be <sub>2</sub> O <sub>3</sub> .*	Cs <sub>2</sub> O.	Fe <sub>2</sub> O <sub>3</sub> .	
70·00	26·33	3·31	0·88	0·40	= 100·92

The Elba specimen is distinguished from those hitherto analysed, in containing a small percentage of glucina, a large amount of alumina, as well as by the presence of cæsia.

W. F.

**Tourmaline from the Island Giglio.** By E. BECHI (Jahrbuch für Mineralogie, 1872, 95).

A SPECIMEN of black tourmaline of great beauty from the granite of Giglio had a specific gravity 3·15 and the following composition :—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	B <sub>2</sub> O <sub>3</sub> .	F.
36·71	31·57	9·30	8·51	0·64	0·49	2·83	0·70	5·56	1·85=98·16

This tourmaline is remarkable for its large percentage of iron protoxide.

W. F.

**Native Phosphates of Lime.** By T. PETERSEN (Jahrbuch für Mineralogie, 1872, 96).

THE author points out the support given to his view of regarding staffelite as a distinct species, by the results of an examination of a Cornish francolite by Maskelyne and Flight, and proposes that the name staffelite should be applicable to all basic phosphates of the form  $\text{Ca}_3\text{P}_2\text{O}_8 + x\text{CaH}_2\text{O}_2$  ( $x$  being about 1), in which the calcium in excess of that united with phosphoric acid is in combination with fluorine and carbonic acid, and the water of hydration is still entirely or partially present. He gives an analysis of a yellow earthy phosphorite from Katzenellenbogen in Nassau.

SiO <sub>2</sub> .	P <sub>2</sub> O <sub>5</sub> .	CO <sub>2</sub> .	F.	I (and Cl).	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	H <sub>2</sub> O.
1·76	37·04	2·48	4·27	0·09	2·51	52·07	0·26	2·23=102·71
Deduct oxygen, equivalent to fluorine and iodine.....								1·81

100·90

besides traces of sulphuric acid, alumina, chromium oxide, soda and potash. It will be remarked that this phosphorite, like staffelite, contains considerable quantities of fluorine, carbonic acid, and water.

W. F.

\* Or GlO.

**The Permian Rocks of the Lower Odenwald.** By E. COHEN  
(Jahrbuch für Mineralogie, 1872, 98).

THIS elaborate paper contains the results of a chemical examination of several of the rock-specimens of the older porphyries. The author examined :

I. Felsite porphyry, with but few disseminated particles, from the rothliegende (lower Permian) of Handschuchsheim.

II. Felsite porphyry, containing an abundance of disseminated particles from the same locality.

III. Felsite porphyry from Leichtersberg.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	CO <sub>2</sub> .
I....	75.39	12.92	1.71	0.85	0.65	0.61	5.34	2.06	1.21	— = 100.74
II ..	73.80	11.60	1.90	0.60	1.20	0.70	7.50	1.40	1.20	1.60 = 101.50
III..	75.78	12.16	1.77	0.51	0.79	0.25	6.28	1.16	1.39	— = 100.09

The middle rothliegende at Olberg, near Schriesheim, contains siliceous tufa (iv), very compact and homogeneous in structure, and of a beautiful leek-green colour, characters that have not unfrequently gained for it the name of plasma, which it undoubtedly resembles. The upper rothliegende likewise contains tufas in considerable amount; one (v) consisting of a bright violet magma, containing fragments of porphyry, quartz-granules, felspar, and white mica, was examined.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	CO <sub>2</sub> .
IV..	82.47	9.55	0.43	0.57	0.53	trace	4.69	0.58	1.18	— = 100.00
V ..	72.91	17.70	1.20	0.44	0.13	0.28	5.37	1.85	0.12	= 100.00

The later porphyry overlying the rothliegende is distinguished from the older porphyry by the fineness of its disseminated particles, the absence of mica, the presence of magnetite, and a tendency to assume a chondritic structure.

Two specimens (i) from Apfelskopf, near Ziegelhausen, and (ii) from Edelstein, near Schriesheim, gave the following numbers:—

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.
I....	74.55	13.56	0.34	1.16	0.47	0.38	6.14	2.45	1.74 = 100.79
II ..	73.22	16.33	1.37	0.70	0.85	—	5.65	0.84	1.29 = 101.25

Overlying the seam of heavy spar at Schriesheim, is a bed apparently of porphyry; the author found it, however, to be a quartz rock enclosing fragments of granite and felspar, and having the following composition:

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.
	94.756	3.198	1.066	0.076	0.278	0.005	0.001	0.003	0.690 = 100.073

W. F.

**The Meteoric Iron of Ovifak, Greenland.** By F. WÖHLER  
(Ann. Chem. Pharm., clxiii, 247).

NEAR the large iron masses which Nordenskiöld has already described (p. 603 of this volume), were found other iron in grains and spherular

masses, and a vein of the metal several inches wide and some feet in length, enclosed in a rock that is apparently trap, but shows a marked difference in composition from the basalt-breccia, from which it protrudes. The metal of the vein which Wöhler has examined, resembles grey cast iron; it has a bright lustre, is very hard, quite unalterable in air, and has a specific gravity of 5.82. Nordenskiöld obtained gas from the metal of the larger masses by heating them; Wöhler finds that the iron of the vein evolves more than 100 times its volume of a gas which burns with a pale blue flame, and is carbonic oxide mixed with a little carbonic acid. The "iron," in fact, contains a considerable amount of carbon and a compound of oxygen, and has evidently not been at any time exposed to a high temperature. By heating, the iron becomes brighter in appearance, and though more soluble in acid, still leaves a carbonaceous residue. However, a fragment heated in hydrogen lost 11.09 per cent., or, in other words, was shown to contain that amount of oxygen. Hydrochloric acid acts but slowly and partially on this metal, evolving sulphuretted hydrogen and then hydrogen possessing the odour of a hydrocarbon, and leaves a black granular magnetic powder which, though insoluble in acid when cold, generates on the application of heat a gas with a strong odour of a hydrocarbon, and leaves a residue of amorphous sooty carbon and slightly lustrous graphitic particles. In ferric chloride the "iron" dissolves without evolution of gas, leaving about 30 per cent. of a black residue which, after having been dried at 200°, lost by subsequent ignition in hydrogen 19 per cent. of its weight, water being found. This is very readily attacked by acid, evolves sulphuretted hydrogen, and leaves a residue of nearly pure carbon in powder and graphitic scales. Ferric chloride and hydrogen chloride appear, therefore, to remove the free metal only, and to be without action on its compounds with sulphur and oxygen. The "iron" has the following ultimate composition:—

Iron.	Nickel.	Cobalt.	Phosphorus.	Sulphur.	Carbon.	Oxygen.	
80.64	1.19	0.49	0.15	2.82	3.69	11.09	= 100.07

Wöhler was disposed to regard the oxygen, constituting so considerable a part of an apparently metallic mass, as present in the form of a diferrous oxide,  $\text{Fe}_2\text{O}$ , were it not that this view provides no iron for combination with sulphur and carbon. As Nordenskiöld found magnetite in other Ovifak irons, Wöhler regards that constituting the veins as an intimate mixture of magnetite, of which there would be 40.2 per cent., with metallic iron, its sulphide, carbide, and phosphide, its alloys with nickel and cobalt, and some carbon in isolated particles. The latter undergoes no change when the magnetite and carbide, by the action of heat, generate carbonic oxide.

W. F.

### Gases occluded in Meteoric Iron from Augusta Co., Virginia.

By J. W. MALLETT (Proc. Roy. Soc., xx, 365; Chem. News, xxv, 292).

THE iron was very carefully cut in a planing machine, and the piece obtained was heated in a porcelain tube connected with a Sprengel pump.



The iron weighed 124·589 grams., having a volume of 15·87 c.c. 36·33 c.c. of gas. at 0° C. and 760 mm. pressure were obtained during fourteen and a-half hours, the greater portion coming off during the first two and a-half hours.

The analysis of the gas gave the following results:—

Hydrogen .....	35·83
Carbonic oxide .....	38·33
Carbonic anhydride ....	9·75
Nitrogen .....	16·09

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100·00

Comparing these results with those obtained by Graham in analysing the gases occluded in Lenarto iron, it is seen that the hydrogen in the Virginia iron is much less than in the other specimen, the carbonic oxide is much higher; Graham's analysis shows no carbonic anhydride. Graham, in his paper read to the Royal Society, said that a large amount of carbonic oxide occluded in iron pointed to a telluric origin for that iron. The author is of opinion that the Virginia iron is undoubtedly meteoric, and suggests that it may have come from a different atmosphere to that from which the Lenarto iron came.

M. M. P. M.

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**Gases enclosed in Coal.** By Dr. ERNST VON MEYER (J. pr. Chem. [2], v, 144—183).

THE gases actually enclosed in coal not having as yet been subjected to any thorough examination, the author, at the suggestion of Professor Kolbe, has undertaken a series of experiments to supply this deficiency, and thereby to throw some light on the natural history of coal.

The gases employed in this research were obtained from the coals by introducing two to four hundred grams of the latter into a flask, which was immediately filled up with hot de-aërated water, which was then boiled so as to expel the gases from the coal and drive them through a short straight tube, fitted by a caoutchouc plug to the mouth of the flask, into a number of tubes inverted in a basin of water supported on the end of the tube proceeding from the flask. The gases so collected were analysed by Bunsen's methods; the data connected with the determinations so made are given in full in the original paper.

Coals from several districts were examined, both when freshly raised and after having been exposed to the influence of the weather for times varying from one to several years. The results obtained, though of great interest, may be very briefly summarised.

The majority of coals gave by this treatment gases agreeing in composition with those known to occur in ordinary mine-gas, that is, carbonic acid, oxygen, nitrogen, and marsh-gas.

The quantity of gas contained in various coals freshly raised and long weathered, is shown by the following table (Mem., the indication numbers attached to the name of the coal will be retained throughout the abstract to indicate the same sample):—

		100 grams of	
		Freshly raised.	Weathered.
(1).	Zwickau coal gave .....	38.0 c.c.	(a) 18.0 c.c.
(2).	" " " .....	25.5 "	(a) 18.6 "
(3).	" " " .....	54.8 "	(a) 13.6 "
(4).	Westphalian, from Essen .....	22.5 "	
(5).	" " Bochum ..	50.6 "	(a) 43.2 "
(6).	" " " ..	54.4 "	(a) 39.2 "

The composition of these gases presents peculiarities in two cases only, viz., 1 (a) and 3 (a), to which we will return, and which, it is to be observed, are both from coals altered by weathering.

The composition of the gases from fresh coal is shown by the following table:

	CO <sub>2</sub> .	O.	N.	CH <sub>4</sub> .
1.....	2.42	2.51	23.17	71.9
2.....	4.02	0.62	50.36	45.00
2 (a) ..	2.25	0.7	23.89	73.16
3.....	0.6	trace	48.0	51.4
4.....	7.5	2.59	89.91	—
5.....	4.87	2.66	75.82	16.65
5 (a) ..	11.12	2.88	78.6	7.4
6.....	1.30	1.60	66.85	30.25
6 (a) ..	4.35	3.35	81.18	11.12

These numbers selected from those given show that exposure to the weather causes a loss of a great part of the marsh-gas, as was to be expected, but the ratio of oxygen to nitrogen and carbonic acid also serves to show that in the process of the passage of vegetable remains into coal, the oxygen of the air concerned has gone mostly to the burning of the hydrogen, leaving the carbon comparatively intact.

The gas obtained from 1 (a) and 3 (a) was quite different in composition from that obtained from any other specimen—the figures of the analysis speak for themselves:

	CO <sub>2</sub> .	O.	N.	CO.	CH <sub>4</sub> .	C <sub>2</sub> H <sub>6</sub> .	Absorbed by fuming sulphuric acid.
1 (a) .....	16.7	4.9	55.15	—	3.17	18.61	1.47
Ditto, collected one week later .....	11.4	3.8	60.98	—	3.44	18.88	1.5
Ditto, collected two weeks later than the preceding .....	12.10	1.10	65.16	—	3.19	16.85	1.6
3 (a) .....	7.62	2.44	50.75	—	15.88	22.35	0.96
Ditto, collected one week later .....	10.10	2.6	50.53	1.82	10.18	23.32	1.45
Ditto, collected two months later than the preceding .....	11.18	2.82	67.99	—	—	16.36	1.65

The analytical data obtained (oxygen consumed, contraction, and carbonic acid formed) seemed to leave no doubt that hydride of ethyl was really a constituent of the gas obtained from these coals. The numbers given are in all respects satisfactory.

Three specimens of grey shaley coal containing much pyrites, gave gases characterised by the absence of hydrocarbons, and the preponderance of carbonic acid. As it is well known that coals which contain much pyrites, oxidise more readily than others, the formation of the product of the combustion of carbon can be explained in this case by the greater energy of the oxidising action. The gases in this case had the composition shown—

	CO.	O.	N.
7 .....	48·7	1·8	49·5
8 .....	38·2	1·2	60·6
9 .....	54·9	1·2	43·9

APPENDIX (*J. pr. Chem.* [2], v, 416—427).—Further experiments were made to determine whether exposure of a coal to a continued temperature of 50° C. caused an alteration resulting in further production of gas, or if the gases contained in it underwent any change of composition. The Zwickau coal marked 1 (*a*) on page 799, was taken for these experiments, because its gases had been repeatedly analysed and found to present many points of interest.

The numbers formerly obtained for these gases were—

	CO <sub>2</sub> .	O.	N.	C <sub>2</sub> H <sub>6</sub> .	CH <sub>4</sub> .	Absorbed by fuming sulphuric acid.
( <i>a</i> ) First collected gas ....	16·7	4·9	55·15	18·61	3·17	1·47
( <i>b</i> ) Gas taken a week } later .....	11·4	3·8	60·98	18·88	3·44	1·50
( <i>c</i> ) Two weeks after <i>b</i> ....	12·1	1·10	65·16	16·85	3·19	1·6

After the last of these analyses, the coal lay between three and four months in a cool dry place, when it was found to give off gas of the composition—

CO<sub>2</sub>=12·91, O=2·57, N=57·8, C<sub>2</sub>H<sub>6</sub>=22·62, CH<sub>4</sub>=4·06 per cent.

At the same time as this examination was made, another portion of the coal was kept for two days at 45° C., and then immediately treated in the usual manner, when it evolved gas as rapidly as the unwarmed portion. It was found to be free from marsh-gas.

CO<sub>2</sub>=10·65, O=3·2, N=74·72, C<sub>2</sub>H<sub>6</sub>=9·8, and absorbed by sulphuric acid 1·63 per cent.

By calculation it is shown that the heavy hydrocarbon is probably butylene.

It thus appears that on warming, the whole of the marsh-gas first escapes by reason of its greater diffusibility.

The gases from another coal from Zwickau were also examined both



before and after heating the coal to 50° C. for twenty-four hours. The numbers given for the former include some error of the press, since the percentages given add up to 108. The hydrocarbons present were marsh-gas, hydride of ethyl, and butylene. In the gas from the heated coal, it seems to be shown that some high term of the marsh-gas series, probably hydride of propyl, was present. The analytical numbers agree well with those required by—

$\text{CO}_2=15.6$ ,  $\text{O}=3.10$ ,  $\text{N}=73.33$ ,  $\text{C}_3\text{H}_8=4.39$ ,  $\text{C}_2\text{H}_6=2.06$ ,  $\text{C}_4\text{H}_{10}=1.75$ .

C. H. G.

**Gases Enclosed in English Coal.** By Dr. ERNST VON MEYER  
(J. pr. Chem. [2], v, 407—416).

IN this paper the author gives the results of the examination of the gases obtained from eight samples of coal from the Newcastle and Durham districts.

No. 1. Low Main seam, from Bewicke Main Colliery (Newcastle district).

No. 2. Maudlin seam, from Bewicke Main Colliery (Newcastle district).

No. 3. Main coal seam, Urpeth Colliery, Newcastle (Durham district).

No. 4.  $\frac{5}{4}$ -seam, Urpeth Colliery, 30 fathoms from surface.

No. 5.  $\frac{5}{4}$ -seam, Wingate Grange Colliery, Durham district, 74 fathoms from surface.

No. 6. Low main seam, Wingate Grange Colliery, 108 fathoms from surface.

No. 7. Harvey seam, Wingate Grange Colliery, 148 fathoms from surface.

No. 8. Harvey seam, Emily Vil., Woodhouse Close Colliery, 25 fathoms from surface; district not given.

From the following table it will be seen that no other hydrocarbon than marsh gas was found in any case:—

No. of Analysis.	District.	$\text{CO}_2$ .	$\text{CH}_4$ .	O.	N.	100 grm. gave — c.c. gas.
1 .....	Newcastle .....	5.55	6.52	2.28	85.65	25.2
2 .....	" .....	8.54	26.54	2.95	61.97	30.7
3 .....	{ Newcastle— Durham .. }	20.86	—	4.83	74.31	27.4
4 .....	" .....	16.51	trace	5.65	77.84	24.4
5 .....	Durham .....	0.34	85.8	trace	13.86	91.2
6 .....	" .....	1.15	84.04	0.19	14.62	238.0
7 .....	" .....	0.23	89.61	0.55	9.61	211.2
8 .....	Unknown .....	5.31	50.01	0.63	44.05	84.0

Taking the specific gravity of coal as 1.3, it will be seen that Nos. 6 and 7 contain nearly three times their volume of gases measured at ordinary pressures, and that therefore as the coal is very hard and dense, the condensation of that gas must be very great.

C. H. G.

## Organic Chemistry.

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**Action of Heat and Pressure on Paraffins.** By T. E. THORPE and J. YOUNG (Deut. Chem. Ges. Ber., v, 556—559).

In a paper read before the Royal Society (March 9, 1871), the authors have shown that when solid paraffin is exposed to a high temperature in a closed vessel, it is almost completely resolved, with evolution of but little gas, into liquid hydrocarbons. This conversion is readily effected on a small scale by sealing up a few grams of solid paraffin into a U-tube of hard glass, which is surrounded by wire gauze. The limb containing the paraffin is gently heated in a combustion furnace, and as soon as it has distilled over, the gas is turned down, the tube when cold is reversed, and the paraffin distilled again; on repeating this process, the paraffin becomes softer and softer, and at last remains liquid. When solid paraffin is heated under the common pressure in a vessel connected with inverted condensers, it is not altered, and further, it appears that only the higher members of the paraffin series undergo this decomposition. Thus a mixture of paraffins and olefines boiling at about  $225^{\circ}$ , was not at all changed by treating it as above described.

In order to get an insight into this reaction, the experiment was performed on a large scale. The paraffin used was obtained from shale; it melted at  $46^{\circ}$ , and its composition was  $C = 85.14$ ;  $H = 14.81$ .  $3\frac{1}{2}$  kilograms yielded 4 litres of liquid hydrocarbons, boiling at—

Below $100^{\circ}$ ..	0.3 litres
„ $100^{\circ}$ — $200^{\circ}$	1.0 „
„ $200^{\circ}$ — $300^{\circ}$	2.7 „
	4.0 „

The residue in the retort solidified on cooling; by repeated recrystallisation from ether it was obtained with the constant melting point  $41.5^{\circ}$ , and containing  $C = 85.19$ ,  $H = 15.34$ . It was not acted upon by bromine, and when heated in a closed tube it yielded liquid hydrocarbons, consisting of a mixture of paraffins and olefines.

By submitting the four litres of liquid to a systematic fractional distillation in Warren's apparatus, the following fractions were obtained:—

$35^{\circ}$ — $37^{\circ}$	$122^{\circ}$ — $125^{\circ}$	$193^{\circ}$ — $195^{\circ}$	$252^{\circ}$ — $255^{\circ}$
$65^{\circ}$ — $70^{\circ}$	$145^{\circ}$ — $148^{\circ}$	$212^{\circ}$ — $215^{\circ}$	$273^{\circ}$ — $276^{\circ}$
$94^{\circ}$ — $97^{\circ}$	$170^{\circ}$ — $172^{\circ}$	$230^{\circ}$ — $235^{\circ}$	$290^{\circ}$ — $295^{\circ}$

The separate fractions consisted of a mixture of olefines and paraffins, which were separated by means of bromine. In the portions below  $200^{\circ}$ , the members of the two series were present in about equal proportions, but in the liquids of the higher boiling points the paraffins preponderated. The following paraffins were isolated:—

	Boiling-point.
Pentane, $C_5H_{12}$ .....	35°—37°
Hexane, $C_6H_{14}$ .....	67°—68°
Heptane, $C_7H_{16}$ .....	97°—99°
Octane, $C_8H_{18}$ .....	122°—125°
Nonane, $C_9H_{20}$ .....	147°—148°

The brominated products obtained were:—

	Boiling-point.
$C_5H_{10}Br_2$ ....	184°—188°
$C_6H_{12}Br_2$ ....	195°—200°
$C_7H_{14}Br_2$ ....	Decomposed when heated.
$C_8H_{16}Br$ ....	185°—190°
$C_9H_{17}Br$ ....	208°—212°

The chloride,  $C_8H_{16}Cl_2$ , boils at about 235° with decomposition.

The decomposition which solid paraffin undergoes is probably similar to that by which butane is resolved into ethane and ethene.

C. S.

**Compounds derived from Paraffin.** By P. CHAMPION (Compt. rend., lxxiv, 1575—1577).

BESIDES repeating and confirming the experiments of Bolley (*Ann. Chem. Pharm.*, cvi, 230), Brodie (*Phil. Trans.*, 1848), Gill and Meusel (*Chem. Soc. Jour.* [2], vi, 466) as to the action of chlorine and bromine upon paraffin, the author obtained from Boghead paraffin, by acting on it for sixty hours with nitro-sulphuric acid at 90°, a yellow transparent oil, (*vide* Schorlemmer, *Proc. Roy. Soc.*, xvi, 372) of density 1.14, soluble in ether and alcohol, and having an acid character; to which he gives the formula  $C_{26}H_{52}N_2O_{10}$ . By dissolving it in ethylic, methylic, or amylie alcohol, and precipitating with hydrochloric acid, he replaced one atom of hydrogen by an atom of the alcohol-radical.

B. J. G.

**Solvent Power of Liquid Cyanogen.** By G. GORE (Proc. Roy. Soc., xx, 67; Chem. News, xxiv, 303).

HIGHLY dried mercuric cyanide in coarse powder was heated in a stout glass tube furnished with a V-shaped bend, and closed by a gutta-percha plug, tied down with copper wire, the whole being protected by screens. The liquid cyanogen condensed in the bend, which was kept cool by a wet rag, in which had been previously placed the body to be tested for solubility.

*Substances soluble at 15°.*—Camphor, chloral hydrate, solid carbon trichloride, iodine, picric acid, and the disulphide, monochloride, and dichloride of carbon. White phosphorus, cane-sugar, carbon, tetrachloride, and water were only slightly soluble.

*Substances insoluble at 15°.*—Carbon, boron, silicon, sulphur, selenium, zinc, mercury, copper, iron, magnesium, salts, gums, fats, and most inorganic and organic substances.

Iodic acid became pink, cuprous iodide vermilion, ammonium carbo-



nate brown. Moisture and alkalis caused the formation of a brown solid body, probably paracyanogen.

C. G. S.

**On the Nitro-compounds of the Fatty Series.** By V. MEYER and O. STÜBER (Deut. Chem. Ges. Ber., v, 514—518).

*Metallic Derivatives of Nitroethane.*—Sodium-nitroethane,  $C_2H_4NaNO_2$ , may be readily obtained in two ways, either by heating a solution of nitroethane in anhydrous benzene with sodium, or by the addition of an alcoholic soda-solution to nitroethane. The sodium is converted, with violent evolution of gas, into a white powder which, after washing with ether, is the pure substance. In the second case the mixture becomes warm and at once solidifies to a white mass, which simply requires to be washed on the filter with absolute alcohol, and to be dried in the water-bath. The second method of preparation also affords a ready method of detecting nitroethane; owing to the slight solubility of the sodium derivative in cold alcohol even traces of nitroethane yield a precipitate on the addition of an alcoholic soda-solution. Neither alcoholic potash nor alcoholic ammonia produces a precipitate with nitroethane.

Sodium-nitroethane is a white, apparently amorphous powder, which explodes only at temperatures above  $100^\circ$ ; it is extremely soluble in water, acids precipitating unchanged nitroethane from the solution. The aqueous solution is not precipitated on the addition of barium chloride, or lead acetate; mercurous nitrate causes a grey, silver nitrate a white precipitate, the latter rapidly becoming brown and finally black; copper sulphate produces a deep green, ferric chloride a blood-red solution. On the addition of mercuric chloride, the solution solidifies after a short time to a mass of crystalline needles of the composition

$HgCl_2C_2H_4NO_2$ , which may be regarded either as  $Hg \left\{ \begin{array}{c} Cl \\ C_2H_4NO_2 \end{array} \right\}$  or as

$Hg \left\{ \begin{array}{c} C_2H_4NO_2 \\ C_2H_4NO_2 \end{array} \right\} + HgCl_2$ .

*Nitromethane.*—Silver nitrite is acted upon by methyl iodide with even greater violence than by ethyl iodide; moreover the whole of the iodide is converted into nitromethane, and none of the isomeric methyl nitrite is produced. Nitromethane is a heavy oil, of a peculiar odour; it boils at  $99^\circ$ . On treatment with an alcoholic soda-solution, it yields transparent needles of the sodium derivative,  $CH_2NaNO_2$ , the aqueous solution of which gives characteristic precipitates with various metallic solutions.

With regard to the constitution of sodium-nitroethane, the authors are of opinion that the nitro-group and the sodium are united with the same carbon atom, as expressed by the formula,  $\left\{ \begin{array}{c} CH_3 \\ CHNaNO_2 \end{array} \right\}$ , and that the explanation of the non-formation of metallic derivatives from nitro-pentane,  $C_5H_{11}NO_2$  (this Journal, x, 474) may be that this compound contains the  $CNO_2$  group united with three other carbon-atoms, so that there is no hydrogen-atom in the immediate neighbourhood of the  $NO_2$  group.

H. E. A.

**A Third Dichlorinated Propylene.** By C. FRIEDEL and R. D. SILVA (Compt. rend., lxxv, 81—85).

THE two bodies having the formula  $C_3H_4Cl_2$ , already made known by the authors, are simultaneously formed in several reactions. They are produced either by the action of water, or of solid or alcoholic potash upon chlorinated methylchloracetol, or by the action of chlorine on monochlorinated propylene. One of them boils at  $75^\circ$ , the other at  $94^\circ$ ; their constitutional formulæ are:  $CH_3.CCl.CHCl$  and  $CH_2Cl.CCl.CH_2$ .

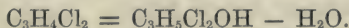
The authors have now examined Reboul's *dichlorhydric glycide*, which has the same composition. From some slight difference in the mode of procedure, his process in their hands yielded very little of this body, the product consisting mostly of the chloride above referred to, boiling at  $94^\circ$ . They obtained, however, the body in question when attempting to prepare a large quantity of pure trichlorhydrin by the action of phosphorus oxychloride upon the dichlorhydrin of glycerin. A bad yield of trichlorhydrin was obtained, but a considerable quantity of Reboul's compound, boiling at  $105^\circ$ — $107^\circ$ , and having a density of 1250 at  $0^\circ$  and 1218 at  $25^\circ$ . It fixes bromine with some energy in diffused light, but with less than that shown by the chloride boiling at  $94^\circ$ . The new bromide boils at  $220^\circ$ — $225^\circ$ , and its density at  $0^\circ$  is 2190 at  $0^\circ$ , and 2147 at  $25^\circ$ : the density of the bromide boiling at  $205^\circ$  is 2161 at  $0^\circ$ , and 2112 at  $25^\circ$ .

The new chlorinated propylene, boiling at  $106^\circ$ , does not combine with hydrogen chloride at  $100^\circ$  or  $150^\circ$ , but is blackened by it; the chlorinated propylene boiling at  $94^\circ$  readily fixes hydrogen chloride at  $100^\circ$ — $105^\circ$ , yielding chlorinated methylchloracetol.

The new chloride yields, when treated with alcoholic potash at  $100^\circ$ , a chlorinated ether,  $C_3H_4ClO.C_2H_5$ , isomeric with that similarly obtained from the chloride boiling at  $94^\circ$ , together with a little propargylic ether. The new ether boils at  $120^\circ$ — $125^\circ$ , and has a density of 1021 at  $0^\circ$ , and 994 at  $25^\circ$ : the ether from the chloride boiling at  $94^\circ$  boils at  $110^\circ$ , and has a density of 1011 at  $0^\circ$ , and 995 at  $21.5^\circ$ . The new ether appears to be identical with that obtained by L. Henry by fixing two atoms of chlorine on ethyl-allyl oxide, and treating the product with alcoholic potash.

It fixes two atoms of bromine with considerable energy, and yields thereby a compound differing from that derived from the chlorinated ether boiling at  $110^\circ$ . The new product boils at about  $220^\circ$ , but with considerable decomposition, turning brown and evolving much hydrogen bromide. The distillate deposits nacreous plates which are unstable and have not been further examined.

The new dichlorinated propylene results from the dehydration of the dichlorhydrin by the phosphoric anhydride formed in the reaction of a part of the dichlorhydrin upon the phosphorus oxychloride—



For on mixing dichlorhydrin, boiling at  $174^\circ$  and obtained by the action of hydrogen chloride upon epichlorhydrin, with phosphoric anhydride, molecule for molecule, and heating gently, it blackens and the whole becomes solid on cooling. On adding water and distilling,

dichlorinated propylene, boiling at  $107^{\circ}$ , passes over. If, as supposed, dichlorhydrin, prepared in the usual way, consists of two isomeric bodies boiling at  $174^{\circ}$  and  $182^{\circ}$ , the latter is probably identical with the product obtained by Tollens and Henninger by fixing chlorine on allylic alcohol. As it was important for determining the constitution of the new chlorinated propylene, to ascertain whether the latter dichlorhydrin would also yield it, some of the dichloride of allylic alcohol was prepared and treated with phosphoric anhydride. Dichlorinated propylene was not obtained, so that it may be concluded that dichlorhydrin glycide can only be derived from the dichlorhydrin resulting from the fixation of hydrogen chloride by epichlorhydrin.

The following constitutional formulæ are therefore suggested. They rest upon the supposition that allylic alcohol is  $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\text{OH}$ . They do not agree with those of Henry, or with those of Hübner and Müller for the two dichlorhydrins. All these bodies, as well as the chloride  $\text{CH}_2\cdot\text{CH}\cdot\text{CHCl}_2$  derived from acrolein, are referrible to the propylene type,  $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_3$ .

*Dichlorinated Propylenes.*

Boiling-point, $76^{\circ}$ .	Boiling-point, $94^{\circ}$ .	Boiling-point, $106^{\circ}$ .
1.	2.	3.
$\text{CH}_3$   $\text{CCl}$    $\text{CHCl}$ .	$\text{CH}_2\text{Cl}$   $\text{CCl}$    $\text{CH}_2$ .	$\text{CH}_2\text{Cl}$   $\text{CH}$    $\text{CHCl}$ .

*Chlorinated Ethers and Brominated Derivatives, corresponding to the Chlorinated Propylenes 2 and 3.*

2.		3.	
$\text{CH}_2(\text{OC}_2\text{H}_5)$   $\text{CCl}$    $\text{CH}_2$ .	$\text{CH}_2(\text{OC}_2\text{H}_5)$   $\text{CClBr}$   $\text{CH}_2\text{Br}$ .	$\text{CH}_2(\text{OC}_2\text{H}_5)$   $\text{CH}$    $\text{CHCl}$ .	$\text{CH}_2(\text{OC}_2\text{H}_5)$   $\text{CHBr}$   $\text{CHClBr}$ .

*Dichlorhydrins.*

From epichlorhydrin.	From allylic alcohol.
$\text{CH}_2\text{Cl}$ $\text{CH}(\text{OH})$ $\text{CH}_2\text{Cl}$ .	$\text{CH}_2\text{Cl}$ $\text{CHCl}$ $\text{CH}_2(\text{OH})$ .

E. D.

**Reduction-products of Silicic Ether.** By A. LADENBURG (Deut. Chem. Ges. Ber., v, 565).

SILICOHEPTYL-ETHYL ether, treated with zinc-ethyl and sodium, forms silicium-ethyl boiling at about  $150^{\circ}$  and insoluble in sulphuric acid; also *silicoheptyl hydride*,  $\text{Si}(\text{C}_2\text{H}_5)_3\text{H}$ , a colourless liquid boiling at  $107^{\circ}$ ,



and smelling like the petroleum hydrocarbons; its sp. gr. at  $0^{\circ}$  is 0.751, and it gave 118.5 as vapour-density, the calculated value being 116.

The specific gravities at  $0^{\circ}$  of the ethyl and oxethyl silicium compounds exhibit a regular increase as the oxygen present is larger; thus:—

Silicium ethyl, $\text{Si}(\text{C}_2\text{H}_5)_4$ .....	0.8341
Silicoheptyl ethyl-ether, $\text{Si}(\text{C}_2\text{H}_5)_3(\text{O.C}_2\text{H}_5)$ ....	0.8414
Silicium diethyl-ether, $\text{Si}(\text{C}_2\text{H}_5)_2(\text{O.C}_2\text{H}_5)_2$ ....	0.8752
Orthosilicopropionic ether, $\text{Si}(\text{C}_2\text{H}_5)(\text{O.C}_2\text{H}_5)_3$ ..	0.9207
Silicic ether, $\text{Si}(\text{OC}_2\text{H}_5)_4$ .....	0.9676

Silicoheptyl hydride is readily acted on by bromine, with formation of *silicoheptyl bromide*,  $\text{Si}(\text{C}_2\text{H}_5)_3\text{Br}$ , boiling between  $159^{\circ}$  and  $163^{\circ}$ ; with dilute ammonia this bromide forms triethylsilicol and silicoheptyl oxide; with potash only the latter. Fuming nitric acid attacks the hydride, wherein it differs from silicium-ethyl. Fuming sulphuric acid appears to give a sulphonic derivative destroyed by water; on diluting the sulphuric acid, an oil rises to the top; this consists chiefly of silicoheptyl oxide,  $\text{Si}(\text{C}_2\text{H}_5)_6\text{O}$ , but a little silicium diethyl oxide,  $\text{Si}(\text{C}_2\text{H}_5)_2\text{O}$ , appears to be also formed, and also a little triethylsilicol. Silicoheptyl oxide dissolves in concentrated sulphuric acid, and this solution, on decomposition by water, gives a little triethyl silicol and much unaltered silicoheptyl oxide: whence it appears that silicoheptyl oxide and alcohol exhibit the same relations as ethyl-oxide and alcohol, the latter giving the former by treatment with sulphuric acid, and the former, by long-continued action of sulphuric acid, giving ethylsulphuric acid, which is decomposed by distillation with water, forming alcohol.

C. R. A. W.

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**Propargyl Alcohol.** By L. HENRY (Deut. Chem. Ges. Ber., v, 569).

MONOBROMINATED allyl alcohol and aqueous caustic potash form propargyl alcohol: sodium also produces the same substance. It is a colourless liquid of peculiar odour, boiling at  $110^{\circ}$ — $115^{\circ}$  at 762 mm., or about  $30^{\circ}$  higher than its ethylic ether ( $82^{\circ}$ — $85^{\circ}$ ); while allyl alcohol and allyl-ethylic ether show about the same difference ( $96^{\circ}$ — $97^{\circ}$  and  $60^{\circ}$ — $65^{\circ}$  respectively): its specific gravity is 0.9628 at  $21^{\circ}$ , and its vapour-density 1.88 (calculated 1.93): it is readily decomposed by electronegative chlorides, bromides, &c., and combines with  $\text{Br}_2$  or  $\text{HBr}$ , like unsaturated compounds generally; like allylene, it precipitates ammoniacal copper and silver solutions, giving compounds of formulæ  $\text{C}_3\text{H}_2\text{Cu}.\text{OH}$  and  $\text{C}_3\text{H}_2\text{Ag}.\text{OH}$ : the author regards it as a *primary* alcohol,  $\text{CH}\equiv\text{C}-\text{CH}_2.\text{OH}$ .

C. R. A. W.

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**On Cholesterin.** By O. LOEBISCH (Deut. Chem. Ges. Ber., v, 510—514).

THE author has oxidised cholesterin by boiling it for twelve hours with potassium dichromate and sulphuric acid, and has isolated a white,

amorphous, acid product, to which he assigns the formula  $C_{24}H_{40}O_6$ . At the same time a small quantity of a mixture of several lower fatty acids, probably consisting of acetic, propionic, and butyric acids, was obtained. Barium, calcium, and silver salts, containing the equivalent quantity of these metals in place of two atoms of hydrogen, were prepared by precipitation from an ammoniacal solution of the acid.

A comparison of the formula of the new acid with that of cholic acid,  $C_{24}H_{40}O_5$ , shows that it may be regarded as an oxycholic acid. It is not affected by treatment with sodium amalgam in alkaline solution; on fusion with potassium hydrate it is oxidised with great difficulty, and only secondary decomposition-products are obtained, viz., inflammable gases, a brown insoluble substance, and lower fatty acids.

In further proof of the alcoholic nature of cholesterin, the author has prepared the following derivatives:—

*Acetyl-cholesteryl*,  $C_{26}H_{43}(C_2H_3O)O$ , by treating cholesterin with acetyl-chloride; it crystallises in small colourless needles, which melt at  $92^\circ$ .

*Cholesterylamine*,  $C_{26}H_{43}.NH_2$ . The chloride obtained by the action of phosphorus pentachloride on cholesterin, is readily converted into this compound by digestion with alcoholic ammonia. It crystallises in small plates, melting at  $104^\circ$ .

The following series of cholesterin derivatives are now known:—

$C_{26}H_{43}.OH$ . . . . .	Cholesterin.
$C_{26}H_{43}.ONa$ . . . . .	Sodium cholesterylolate.
$C_{26}H_{43}.OC_2H_3O$ . . . . .	Acetylcholesteryl.
$C_{26}H_{43}.Cl$ . . . . .	Cholesteryl chloride.
$C_{26}H_{43}.NH_2$ . . . . .	Cholesterylamine.

H. E. A.

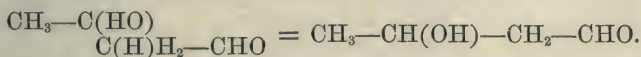
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**Note on an Aldehyde-Alcohol.** By A. WURTZ (Compt. rend., lxxiv, 1361—1367).

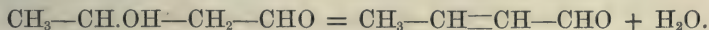
THIS compound,  $C_4H_6O_2$ , which plays the part both of an alcohol and an aldehyde, is polymeric with ordinary aldehyde, and is formed when the latter is mixed with an equal volume of water and two volumes of hydrochloric acid. The colourless liquid gradually assumes a fawn-coloured tint on standing, whilst the odour of aldehyde becomes more feeble. It is now neutralised with sodium carbonate and agitated with ether, which takes up the new compound and leaves it on evaporation as a transparent liquid. This, when purified by rectification under a pressure of 20 mm., passes over as a colourless liquid to which the author has given the name of *aldol*. It has a sp. gr. of 1.1208 at  $0^\circ$ , and is then quite viscous, but becomes as fluid as water on being gently heated. It has a high refractive power, and mixes in all proportions with water or alcohol. It is also soluble in ether and has an aromatic bitter taste. Under a pressure of 20 mm. it distils at about  $90^\circ$ , but when heated to  $135^\circ$  under the ordinary atmospheric pressure, it decomposes, yielding water and crotonic aldehyde. A similar decomposition takes place when it is heated with acetic acid. Aldol reduces ammoniacal silver nitrate and cupropotassic solution. It combines with acetic anhydride, forming two acetates, which distil under a pressure of

20 mm., the one between  $100^{\circ}$  and  $110^{\circ}$ , and the other between  $150^{\circ}$  and  $160^{\circ}$ . The former  $\text{C}_4\text{H}_7\text{O}(\text{C}_2\text{H}_3\text{O}_2) = \text{CH}_3-\text{CH}(\text{OC}_2\text{H}_3\text{O})-\text{CH}_2-\text{CHO}$ , is a colourless liquid insoluble in water, but soluble in alcohol. Heated with water to  $100^{\circ}$ , it decomposes with formation of acetic acid. The latter,  $\text{C}_4\text{H}_6(\text{C}_2\text{H}_3\text{O}_2)_2$ , which may be considered as the diacetate of crotonic aldehyde, is a thick liquid, insoluble in water and decomposed when heated with it, yielding acetic acid. Nitric acid attacks aldol with great energy, giving rise to ordinary aldehyde and several acids, amongst which is oxalic acid. Sodium amalgam gives resinous products, but if the solution be kept acid, other substances are produced which may be extracted by agitation with ether. These have not yet been examined. The action of hydriodic acid produces a thick oily liquid which is very alterable. Phosphorus perchloride acts very energetically on aldol, with formation of phosphorus oxychloride and a chlorinated body which could not, however, be obtained in a state of purity.

From its mode of formation and these reactions, especially the facility with which it splits up into crotonic aldehyde and water, the author considers aldol to be  $\text{CH}_3-\text{CH}(\text{OH})-\text{CH}_2-\text{CHO}$ , formed from two molecules of aldehyde, thus:—

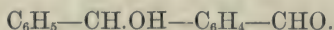


Its decomposition into water and crotonic aldehyde would then be represented by the equation:—



Aldol is not the only product of the condensation of aldehyde under the influence of hydrochloric acid; for if the mixture be allowed to stand until it acquires a brown tint and opaline appearance, and is then neutralised and treated with ether as previously described, the ethereal solution leaves nacreous plates which may be separated from the mother-liquor by means of Bunsen's vacuum filter. The substance thus obtained distils at  $137^{\circ}$  under a pressure of 20 mm., forming a colourless mass, soluble in alcohol and ether. Boiling water likewise dissolves it, and deposits it on cooling in crystals which melt at  $155^{\circ}$ . This compound,  $\text{C}_8\text{H}_{14}\text{O}_3 = (\text{C}_4\text{H}_7\text{O})_2\text{O}$ , which has strongly marked reducing powers, is the anhydride of aldol, and has probably the same relation to aldol that ether has to alcohol.

In its power of forming combinations with acids, aldol resembles the sugars, and like glucose possess the properties both of an aldehyde and of an alcohol. It is possible, therefore, that formic aldehyde may be produced in the process of vegetation, and by the condensation of several of its molecules, give rise to these hydrates of carbon. The author has commenced some experiments on the action of hydrochloric acid on formic aldehyde, and concludes by observing that as benzoïn is formed by the condensation of two molecules of benzoic aldehyde, its formula would be—



if the reaction occurred in the same manner as with aldol.

C. E. G.



**On Condensed Aldehydes with Elimination of Water, or Aldanes.** By J. RIBAU (Compt. rend., lxxv, 98—100).

It has long been known that the aldehydes, under the influence of certain agents, give rise to condensation-products. The present communication deals with a new method of obtaining these condensation-bodies, and also with a description of two new products of condensation. The method consists in the action of sodium or zinc on the aldehydes.

Metallic sodium acts in an ethereal solution of acetic aldehyde, kept cool, with evolution of hydrogen; and on passing a current of hydrochloric acid gas into the liquid, to slight acidification, adding sodium carbonate, and evaporating, aldol (p. 808) is obtained, together with another body which appears to be the anhydride of aldol.

Valeric aldehyde acted on by sodium-amalgam yields a substance boiling at  $190^{\circ}$ , having the composition  $C_{10}H_{18}O$ , or two molecules of the aldehyde minus  $H_2O$ .

The action of sodium being very energetic, the action of zinc-turnings at a higher temperature was tried. Zinc-turnings and acetic aldehyde heated to  $100^{\circ}$  for some hours, yield zinc hydrate and condensed products; amongst these, crotonic aldehyde, a little aldol and a new substance boiling about  $220^{\circ}$  are obtained. This body has the composition,  $C_6H_{10}O_2$ , and may be viewed as 3 molecules of aldehyde minus one of water. It has an odour like that of wild mint, and by prolonged distillation seems to be decomposed, with formation of water and higher condensation-products; it combines with alkaline bisulphites, with disengagement of heat and production of a crystalline compound.

Valeric aldehyde heated with metallic zinc to  $180^{\circ}$ , yields the body  $C_{10}H_{18}O$ , a substance which is difficult to purify, and extremely oxidizable.

Pure oil of bitter almonds is attacked by zinc at a temperature of  $250^{\circ}$  to  $260^{\circ}$ , with abundant formation of zinc oxide; the hydrogen, however, is not evolved, but takes part in the formation of some new substances, which the author is at present engaged in studying. Acetone is not attacked by zinc, even at a temperature of  $290^{\circ}$ . The author proposes to call this class of bodies formed by the condensation of aldehydes with elimination of water, by the generic name of "aldanes," and to add the prefix *di*, *tri*, &c., according as the substance is produced from the condensation of 2, 3, &c., molecules of the aldehydes, thus we should have diacetalthane, triacetalthane, divaleralthane, di-isopropaldane, &c.

A. P.

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**Compounds of Sugar with Lime.** By HORSIN-DÉON (Dingl. Polyt. J., cciv, 165).

It has long been known that a concentrated solution of calcium sucrate becomes turbid by warming, and tribasic calcium sucrate separates out. Peligot has shown that, by a certain amount of concentration, the solution coagulates like white of egg, and that the precipitate entirely disappears on cooling.

The author, after a series of experiments on the subject, arrives at the following conclusions:—

1. If a solution of calcium sucrate do not become turbid at  $100^{\circ}$ , the separation of the tribasic sucrate may be effected by a sufficient addition of water.

2. On adding an excess of sugar to a solution made turbid by warming, no further precipitation is effected by heating to  $100^{\circ}$ .

3. The more lime the solution contains, the greater inclination has it to coagulate at  $100^{\circ}$ ; the less lime, the more concentrated must the solution be for the same purpose.

4. The precipitated sucrate redissolves on cooling, if the solution is sufficiently dilute.

5. When strongly concentrated, the precipitate does not redissolve on cooling; increased addition of water dissolves it only slowly, but sugar-solution more readily.

6. All calcium sucrales possess the power of becoming turbid at  $100^{\circ}$  when sufficiently concentrated, of becoming clear at a mean density of  $10^{\circ}$  to  $11^{\circ}$  Baumé, and again becoming turbid on further dilution.

In presence of great excess of lime, these phenomena are not observed.

The clearing again of the solution is a peculiar property of the calcium sucrate. In a clear cold calcium-sucrate solution of indefinite composition, heat appears to favour the combination of the lime with the smallest possible amount of sugar. The tribasic sucrate is formed, into which compound all the lime enters, leaving the excess of sugar free. The tribasic sucrate is more soluble in cold sugar-water than in hot, the solubility increasing with the degree of concentration (vide 1, 2, and 3). The more lime the solution contains, the less dense does it need to be in order to coagulate. A sucrate solution heated to  $100^{\circ}$  in presence of a large amount of lime is decomposed, and by stronger concentration separates on cooling into a mixture of insoluble tribasic and soluble monobasic sucrate.

The separation of the tribasic sucrate takes place only from very concentrated or very dilute solutions, but not from those of medium density. The compound of 28 lime with 201.5 sugar, coagulates at a density of 1.153, remains clear at 1.077, and coagulates again at 1.065; the sucrate with 28 lime to 171 sugar coagulates at 1.200, remains clear at 1.080, and coagulates again at 1.071. Observations on the densities which differently composed solutions of calcium sucrate must have, in order to coagulate at  $100^{\circ}$ , yielded the following results:—

*With 28 parts of Lime.*

Sugar.	Specific gravity.	Sugar.	Specific gravity.
171 .....	1.071	293 .....	1.050
201.5 .....	1.075	323.5 .....	1.0474
232 .....	1.060	354 .....	1.0460
262.5 .....	1.055	384.5 .....	1.0454

By increasing the sugar, the density at which coagulation of the

solution takes place is observed to diminish, but not proportionally to the increase of sugar.

W. S.

### Action of Water and Heat, or of Heat alone, upon Sugar.

By E. J. MAUMENÉ (Bull. Soc. Chim. de Paris [2], xvii, 442).

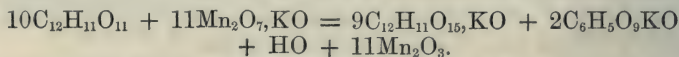
THE author has re-examined inverted sugar, and satisfied himself of the correctness, which has been doubted, of his previous statements. A solution of very pure sugar-candy in five parts of water heated in a water-bath, gradually has its rotatory power reduced to  $0^\circ$  in 27 or 28 hours. Even this *partial* inversion, which is marked by a very feeble yellow discoloration, yields the three products described in the author's previous communications. One of these unites with lime and forms a compound which completely resists the action of carbon dioxide. The sugar yields about half its weight of this substance.

The effects of heat upon dry sugar are also described. In a water-bath it gradually liquefies and becomes converted into barley-sugar. At  $+153^\circ$  it becomes nearly black and yields, among other substances, the author's caramelin,  $C_6H_4O_2$ .

E. D.

### Two New Acids from the Oxidation of Sugar. By E. J. MAUMENÉ (Compt. rend., lxxv, 85—88).

USING the old notation, the author takes the "equivalent" of cane-sugar as 171, and dividing this, according to his theory, by 158, the atomic weight of potassium permanganate, he gets 1.08 as the number of atoms of permanganate acting upon one of sugar, or 11 atoms to 10. These react thus (old notation) :—



The author mixes 200 grams of sugar-candy dissolved in 2 litres of water with the same weight of permanganate dissolved in 4 litres of water, keeping the sugar-solution in rapid rotation during the admixture. In fifteen or twenty minutes the temperature rises  $20^\circ$  or more, and the whole gelatinizes from production of hydrated  $Mn_2O_3$ . The colourless filtrate from this is perfectly neutral, no longer tastes of sugar, and possesses a rotatory power similar and nearly equal to that of the sugar. It gives a white crystalline precipitate with lead acetate which, on treatment with hydrogen sulphide, filtration, and evaporation at a gentle heat, yields the acid,  $C_{12}H_{12}O_{16}$ , which the author names *haeepic acid*. After removal of the lead precipitate, the filtrate gives a second white precipitate with tribasic lead acetate, and this by a similar treatment to that just described, gives the second acid,  $C_6H_6O_{10}$ , which the author names *trigenic acid*.\*

The original filtrate from the manganic hydrate, which is a solution

\* This name was applied by Wöhler and Liebig, five-and-twenty years ago, to the nitrogenised acid  $C_4H_7N_3O_2$ .—E. D.



of the potassium salts of the two acids, gives a slightly soluble crystalline precipitate with calcium chloride; with silver nitrate in the dark, a white precipitate which soon darkens, and when dried and heated, behaves like silver oxalate, but evolves vapours smelling of acetone and burnt sugar. Auric chloride is immediately decomposed. Salts of barium, ferricum, aluminum, and chromium give no precipitates. Ferric chloride is not reduced, even on boiling. Cupric salts give no precipitate in diffused light, but at once yield a green precipitate in direct sunlight. Silver nitrate gives a mirror of silver in direct sunlight.

The mother-liquors of saccharic acid contain these acids.

E. D.

**On the Manna (Eichenmanna, Oak Manna, or Ordinary Manna of the Ash Tree) from Kurdistan.** By F. A. FLÜCKIGER (Arch. Pharm. [2], cl, 159—164).

THE principal constituent of the manna from Kurdistan is a kind of sugar which is contained in it in the crystalline state. It is dissolved by boiling alcohol, and on evaporation to dryness and addition of water, a syrup is obtained which will not again crystallise. It rotates to the right, and reduces in the cold an alkaline cupric solution containing glycerin. The manna contains mucus but no dextrin.

The proportion between the sugar and mucus is very variable; good samples of manna contain over 90 per cent. of sugar. The ordinary officinal manna (*Manna canellata*) contains a kind of mucus which is precipitated by neutral lead acetate, also a second kind of mucus in smaller quantity than the first, which is precipitated by plumbic acetate.

Cane sugar is not contained in the kind of manna worked on.

A. P.

**Action of Acetic Anhydride on Stannic Oxide.** By LAURENCE (Compt. rend., xxiv, 1524—1526).

WHEN two parts of anhydrous acetic acid are heated with one part of stannic (or of metastannic) acid to 150° in a sealed tube, a syrupy liquid is obtained, crystallising on cooling in long needles which, after pressing between blotting paper and drying over lime in vacuo, have the formula,  $\text{SnO}_2 \left( \left\{ \begin{smallmatrix} \text{C}_2\text{H}_3\text{O} \\ \text{C}_2\text{H}_3\text{O} \end{smallmatrix} \right\} \text{O} \right)_2$ .

Washed with anhydrous ether till the washings are free from acid, and dried in vacuo, this substance is converted into a body having the formula,  $\text{SnO}_2 \left( \begin{smallmatrix} \text{C}_2\text{H}_3\text{O} \\ \text{C}_2\text{H}_3\text{O} \end{smallmatrix} \right) \text{O}$ .

The first-named crystals, when exposed to air, become amorphous, and are finally transformed into a vitreous mass of the formula,  $\text{SnO}_2 \left( \begin{smallmatrix} \text{C}_2\text{H}_3\text{O} \\ \text{H} \end{smallmatrix} \right) \text{O}$ .

B. J. G.

**Isobutyric Acid from Citradibromopyrotartaric Acid.** By F. GEROMONT (Deut. Chem. Ges. Ber. [2], v, 492).

KEKULÉ found that monobromocrotonic acid from citradibromopyrotartaric acid yields an acid of the composition of butyric acid when treated with sodium-amalgam and water. From the form, composition, and solubility of the calcium and silver salts, this acid is not butyric but isobutyric acid. From this it results that monobromocrotonic acid from citradibromopyrotartaric acid must be constituted according to one or other of the following formulæ—

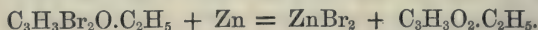


This fact perhaps affords a basis for the study of the constitution of citric acid itself, and of its pyrogenic acids.

E. D.

**Acrylic Acid and Acrylic Ether.** By W. CASPARY and B. TOLLENS (Deut. Chem. Ges. Ber., v. 560).

ETHYL acrylate, which has not hitherto been obtained in a pure state, is easily produced by the action of zinc and sulphuric acid on an alcoholic solution of dibromopropionic ether:—



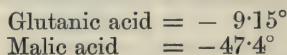
It is a colourless liquid boiling at  $100^\circ$ — $101^\circ$ , and having a most penetrating but not disagreeable odour.

Pure acrylic acid prepared from the lead-salt has a peculiar pungent odour, and boils at  $140^\circ$ — $150^\circ$ . On exposing it to a temperature of  $-15^\circ$ , half of the liquid solidifies to quadratic tables, which, however, could not as yet be separated from the liquid.

C. S.

**Rotatory Power of Glutamic and Malic Acids.** By H. RITTHAUSEN (J. pr. Chem. 354).

THE glutamic and aspartic acids produced by boiling legumin and conglutin with dilute sulphuric acid, yield by the action of nitrous acid glutamic acid and malic acid, which are both optically active, turning the plane of polarisation to the left. The specific rotatory powers of the two bodies were determined with Soleil's saccharometer; calculated with Biot's formula they are found to be—



Pasteur found the rotatory power of active malic acid =  $-5.0^\circ$ .

The rotatory powers of the two acids correspond with that of the mother-substances previously determined—

Glutamic acid	= + 34.7°
Aspartic acid	= + 25.16°.

C. S.

**Reduction of Glutanic Acid by Hydriodic Acid.** By W. DITTMAR (J. pr. Chem. [2], v, 338—353).

*Glutanic acid*,  $C_5H_8O_5$ , a homologue of malic acid, which Ritthausen obtained by the action of nitrous acid upon glutamic acid (*J. pr. Chem.*, xcix, 454; ciii, 233; cvii, 218), is a substance possessing very few characteristic properties. The acid itself forms an indistinctly crystalline mass, and its salts could be obtained only in the amorphous state. But by the action of hydriodic acid it yields a very characteristic reduction-product.

*Deoxyglutanic acid*,  $C_5H_8O_4$ , is produced by heating glutanic acid with four times its weight of concentrated hydriodic acid to 120° for about eight hours. It is very readily soluble in water, alcohol, and ether, and crystallises exceedingly well, forming large, transparent monoclinic crystals, melting at about 97° and decomposing above 280° into water and the anhydride.

*Ammonium deoxyglutamate*,  $C_5H_8O_4 \left\{ \begin{smallmatrix} H \\ NH_4 \end{smallmatrix} \right.$ . On evaporating a strongly ammoniacal solution of the acid under an exsiccator, the acid salt is left behind in transparent concentrically grouped crystals. *Calcium deoxyglutamate*,  $C_5H_8O_4Ca' + H_2O$ , is sparingly soluble in water, and forms opaque laminæ. *Barium deoxyglutamate*,  $C_5H_8O_4Ba' + 5H_2O$ , crystallises in small transparent needles, readily soluble in water. *Lead deoxyglutamate*,  $C_5H_8O_4Pb'$ , is a white heavy precipitate, and the silver salt,  $C_5H_8O_4Ag_2$ , a very bulky precipitate resembling alumina; it is but sparingly soluble in boiling water, and separates on cooling in the crystalline state. It may be obtained in distinct needles by boiling a dilute solution of the acid with silver carbonate; but the greater part of the salt remains behind with the excess of silver carbonate.

Deoxyglutanic acid is isomeric with pyrotartaric acid, from which it follows that glutanic acid is not identical with either of the three homomalic acids derived from aconitic acid, as these latter would yield pyrotartaric acid by reduction.

C. S.

**Oxidation of the Aromatic Hydrocarbons having Lateral Chains.** By POPOFF and ZINCKE (Bull. Soc. Chim., xvii, 500—502).

ALTHOUGH the researches hitherto made on the oxidation-products of these hydrocarbons have accurately determined the number of lateral chains they contain, from a consideration of the nature of the carbonated aromatic acid produced, but little attention has hitherto been directed to the products of the oxidation of the lateral chains themselves. For instance, butylbenzene,  $C_6H_5.CH_2.CH_2.CH_2.CH_3$ , should yield benzoic



acid and propionic acid, whilst isobutylbenzene,  $C_6H_5.CH_2.CH.(CH_3)_2$ , would give benzoic acid and acetone, which by further oxidation would be converted into acetic acid and carbonic anhydride.

The authors have only, as yet, examined the oxidising action of acid potassium chromate and sulphuric acid on amyl-benzene. On cooling, benzoic acid crystallised out, and the solution when distilled gave, besides unaltered hydrocarbon, an acid distillate. This was neutralised with calcium carbonate, and the calcium salts were separated, as far as possible, by fractional crystallisation. From the results obtained, it would appear that the effect of the oxidation was to convert the hydrocarbon employed into benzoic acid and isobutyric acid.

Moreover, as it is thus shown to contain the group isopropyl  $CH(CH_3)_2$ , the amyl in amyl-benzene must have the constitution  $CH_2.CH_2.CH.(CH_3)_2$ , and amylic alcohol the formula,  $CH_2OH.CH_2.CH.(CH_3)_2$ , thus verifying the conclusion arrived at by Popoff when studying the products of the oxidation of the ketone  $C_6H_5.CO.C_4H_9$ .

C. E. G.

**On Aromatic Glycols.** By E. GRIMAUZ (Ann. Chim. Phys. [4], xxvi, 331—355).

By the action of chlorine on boiling xylene from coal-tar, the author and M. Lauth obtained several products of substitution, among which there is a small quantity of a chloride having, as its reactions prove, the constitution  $C_6H_4 \begin{Bmatrix} CH_2Cl \\ CH_2Cl \end{Bmatrix}$  (Bull. Soc. Chim. vii, 233).

Fittig afterwards found that the xylene in coal-tar is a mixture of isomeric dimethyl-benzenes, consisting generally of isoxylene with a smaller quantity of methyl-toluene, and from this it appeared very probable that this dichloride was a derivative of the latter hydrocarbon. This supposition was fully confirmed by further experiments; by passing chlorine into boiling methyl-toluene, which had been produced by synthesis, a large quantity of *tolylene dichloride* was obtained.

*Tolylene Glycol*,  $C_6H_4 \begin{Bmatrix} CH_2OH \\ CH_2OH \end{Bmatrix}$  is readily formed by heating 1 part of the chloride with 30 parts of water for 2—3 hours to  $170^\circ$ — $180^\circ$ . To isolate the glycol, the solution is allowed to evaporate spontaneously at the ordinary temperature, and not on a water-bath, because the hydrochloric acid becoming concentrated, reconverts part of the glycol into the chloride. The concentrated aqueous solution is saturated with potassium carbonate and shaken with ether; the ether is then distilled off, the residue dissolved in boiling water, and the solution filtered through a moist filter. On evaporating this solution *in vacuo*, tolylene glycol crystallises in white, opaque, interlaced needles, melting at  $112^\circ$ — $113^\circ$ , and readily dissolved in water, alcohol, and ether. By heating it with chromic acid solution, it is oxidised to terephthalic acid, the smallest quantity of which can be easily recognised by treating it with a little phosphorus pentachloride, and adding to the product first some methyl alcohol and then a little water, and shaking the whole with ether. On evaporation of the ethereal solution, methyl terephthalate

separates in large crystals, melting at  $140^{\circ}$ . In the same way ethyl terephthalate melting at  $44^{\circ}$  may be obtained.

*Tolylene dichloride*,  $C_6H_4 \begin{Bmatrix} CH_2Cl \\ CH_2Cl \end{Bmatrix}$  is produced not only by the action of chlorine on boiling methyltoluene, but also by distilling the glycol with an excess of hydrochloric acid. It is readily soluble in alcohol, ether, and chloroform, and crystallises, on slowly evaporating the solution, in hard large transparent clinorhombic laminae, melting at  $100^{\circ}$  and boiling at  $240^{\circ}$ — $245^{\circ}$ .

*Nitrotolylene dichloride*,  $C_6H_3(NO_2) \begin{Bmatrix} CH_2Cl \\ CH_2Cl \end{Bmatrix}$  is produced by dissolving the chloride in fuming nitric acid. It crystallises from alcohol in small brilliant laminae, melting at  $35^{\circ}$ , and having an agreeable odour.

*Tolylene dibromide*,  $C_6H_4 \begin{Bmatrix} CH_2Br \\ CH_2Br \end{Bmatrix}$  is formed by adding bromine drop by drop to boiling methyltoluene, and by distilling the glycol with hydrobromic acid. It crystallises from alcohol in small light pearly plates, isomorphous with the chloride, and from chloroform in hard shining crystals melting at  $145^{\circ}$ — $147^{\circ}$ . Heated with water to  $180^{\circ}$ , it is converted into the glycol. In the preparation of this body from the hydrocarbon, higher brominated products are formed at the same time, the vapours of which attack the eyes horribly.

*Tolylene iodide*,  $C_6H_4 \begin{Bmatrix} CH_2I \\ CH_2I \end{Bmatrix}$  is obtained by distilling the glycol with concentrated hydriodic acid. It is readily soluble in ether and chloroform, and crystallises in small rhomboidal plates, melting at about  $170^{\circ}$  with decomposition, and colouring rapidly when exposed to the light.

*Tolylene monobenzoate*,  $C_6H_4 \begin{Bmatrix} CH_2 \cdot OC_7H_5O \\ CH_2 \cdot OH \end{Bmatrix}$ . To prepare this ether, the chloride is heated with an alcoholic solution of sodium benzoate in a water-bath for 24 hours. It crystallises from ether in long fine and light needles.

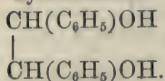
*Tolylene diacetate*,  $C_6H_4 \begin{Bmatrix} CH_2 \cdot OC_2H_3O \\ CH_2 \cdot OC_2H_3O \end{Bmatrix}$  is formed by heating the chloride or bromide with an alcoholic solution of sodium acetate to  $150^{\circ}$  for two hours. It is readily soluble in alcohol and ether, and forms hard colourless crystals melting at  $47^{\circ}$ .

*Tolylene monethyl-ether*,  $C_6H_4 \begin{Bmatrix} CH_2 \cdot OC_2H_5 \\ CH_2 \cdot OH \end{Bmatrix}$ , is produced by boiling the chloride with a concentrated alcoholic potash-solution. It is a limpid liquid of agreeable odour, and boiling at  $252^{\circ}$ . By heating it with benzoyl chloride, a thick oily liquid having an aromatic odour was produced, being probably  $C_6H_4 \begin{Bmatrix} CH_2 \cdot OC_2H_5 \\ CH_2 \cdot OC_7H_5O \end{Bmatrix}$ .

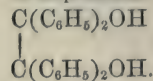
When the chloride or bromide is heated with water above  $200^{\circ}$ , no glycol is formed, but amorphous bodies which are insoluble in all solvents, and as the analysis shows, consist of condensed anhydrides of the glycol.

Tolylene glycol is the first normal primary aromatic glycol known, but there exist also a secondary and a tertiary aromatic glycol, viz. :—

Stilbene glycol, or  
hydrobenzoïn.



Benzopinacone.



Hydrobenzoïn is formed not only by the action of nascent hydrogen on benzaldehyde, and by treating benzoïn with alcoholic potash, but also by mixing it with a quantity of alcohol insufficient to dissolve it, and adding sodium-amalgam; after a few days a clear solution of hydrobenzoïn is obtained.\*

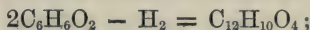
C. S.

**Sappanin.** By J. SCHREDER (Deut. Chem. Ges. Ber., v, 572).

COMMERCIAL extract of sapan wood (*Caesalpinia Sappan*) yields, by fusion with caustic soda, resorcin, a little pyrocatechin, and a crystallisable substance, giving on analysis numbers which agree with the formula,  $\text{C}_{12}\text{H}_{10}\text{O}_4 + 2\text{H}_2\text{O}$ , the water of crystallisation being lost at  $100^\circ$ ; the author terms this compound *sappanin*. It is readily crystallisable from hot water, though almost insoluble in cold water; becomes slightly red-coloured by recrystallisation or by keeping in well-closed vessels, the colour not being removed by animal charcoal, but being completely by zinc and sulphuric acid. Sappanin has no well marked characteristics; it is neutral, soluble in alcohol, ether, and boiling water, and insoluble in chloroform, carbon disulphide, and benzene; it gives (in aqueous solution) a deep cherry-red colour with ferric chloride, and a dark grass green, soon becoming brown, with alkaline hypochlorites; bromine-water colours the liquid brown, and when added in excess causes resinous brown-black flakes to separate. Lead acetate gives a yellowish-white precipitate which becomes coloured and decomposed on drying. Ammoniacal silver solution and Fehling's copper-solution are reduced on warming. For the most part it distils unaltered; nitric acid converts it into styphnic acid; fusing caustic potash and nascent hydrogen produce no change.

Acetyl chloride acts readily at the ordinary temperature, giving a product which is crystallisable from hot alcohol, and hardly soluble in water; this substance gives no colours with ferric chloride or hypochlorites, and appears to be *tetracetyl-sappanin*.

The production of styphnic acid shows that sappanin is a resorcin derivative:—



Not improbably it is related to resorcin in the same manner as diphenyl to benzene:

\* The author gives to benzoïn the formula  $\begin{array}{c} \text{CH}(\text{C}_6\text{H}_5)\text{OH} \\ | \\ \text{CO}(\text{C}_6\text{H}_5) \end{array}$ , and calls it the first

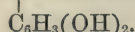
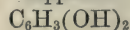
aldehyde of stilbene glycol. But a secondary alcohol cannot form an aldehyde; and as the formula shows, benzoïn is at the same time a ketone and an alcohol.—C. S.



Diphenyl.



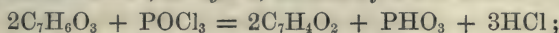
Sappanin.



The author proposes to see if it is producible from monobromoresorcin by the action of sodium. C. R. A. W.

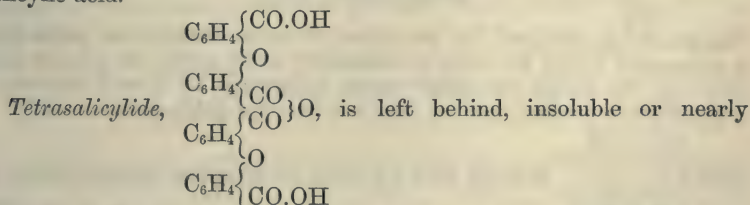
**Anhydrides of Salicylic Acid.** By H. SCHIFF (Ann. Chem. Pharm., clxiii, 218).

SALICYLIC acid dissolves, with evolution of heat, in phosphorus oxychloride, hydrogen chloride going off, and metaphosphoric acid being deposited. After decantation from this deposit and distillation of most of the oxychloride, the residue is decomposed by addition of fragments of ice, and then boiled with water; and the insoluble portion is dried and treated several times with boiling absolute alcohol, which dissolves a crystallisable substance, *salicylide*, formed by the reaction—



This product may be either  $\text{C}_6\text{H}_4 \left\{ \begin{smallmatrix} \text{O} \\ \text{CO} \end{smallmatrix} \right\}$ , or  $\text{C}_6\text{H}_4 \left\{ \begin{smallmatrix} \text{CO} \\ \text{O} \end{smallmatrix} \right\}$ , or

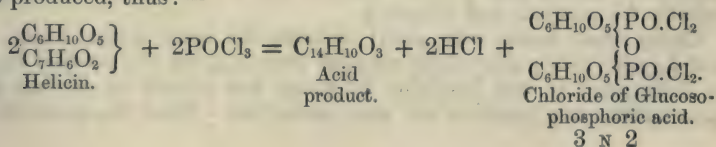
$\text{C}_6\text{H}_4 \left\{ \begin{smallmatrix} \text{CO—O} \\ \text{O—CO} \end{smallmatrix} \right\} \text{C}_6\text{H}_4$ ; it is insoluble in water, gives no iron reaction and no lead precipitate, and is not readily acted on by acetyl chloride; it begins to melt at  $195^\circ$ — $200^\circ$ , with partial decomposition, and becomes wholly fluid at  $220^\circ$ — $225^\circ$ ; with boiling potash it forms salicylic acid.



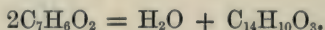
so in the boiling absolute alcohol; it gives no iron reaction, but precipitates lead acetate. Warm concentrated sulphuric acid converts both salicylide and tetra-salicylide into sulphosalicylic acid, which colours iron chloride claret-red and not violet.

Nitrosalicylic acid and phosphorus oxychloride give a resinous product insoluble in water, soluble in alcohol, and reproducing nitrosalicylic acid on boiling with acids or alkalis.

When helicin is treated at the ordinary temperature with phosphorus oxychloride, hydrogen chloride is evolved, and a red condensation-product of salicylic aldehyde and the chloride of glucoso-phosphoric acid are produced, thus:—



This red product may be viewed as formed by dehydration of salicylic aldehyde, thus :—



But its formula is somewhat doubtful, as its purification is difficult, owing to its ready oxidizability when in alkaline solution, treatment with alkalis being necessary to free it from phosphoric acid, which adheres to it with great pertinacity. The same red substance is formed by treating salicylic aldehyde with phosphorus oxychloride, but the red product of salicin and sulphuric acid or phosphorus oxychloride is different.

The glucosophosphoric acid chloride simultaneously produced has been examined by Amato; it yields the acid  $\text{C}_6\text{H}_{10}\text{O}_5 \left\{ \begin{array}{l} \text{PO}(\text{OH})_2 \\ \text{O} \end{array} \right.$  on decomposition with water; the salts of this acid are soluble in alcohol; the sodium salt precipitates neither barium chloride nor lead acetate, and does not give the ordinary phosphoric acid and glucose reactions till after decomposition by heating with sulphuric acid. Ethyl iodide has no action on its lead salt.

C. R. A. W.

**Gallic Acid and Gallic Ether.** By H. SCHIFF (Ann. Chem. Pharm., clxiii, 209).

NACHBAUR has obtained, by the action of acetyl chloride on gallic acid, a compound which he views as tetracetyl-gallic acid; the author finds that by the action of either acetic anhydride or acetyl chloride, a crystallisable product results, which is *triacetyl-gallic acid*.

$\text{C}_6\text{H}_2 \left\{ \begin{array}{l} \text{CO.OH} \\ \text{O.C}_2\text{H}_3\text{O} \\ \text{O.C}_2\text{H}_3\text{O} \\ \text{O.C}_2\text{H}_3\text{O} \end{array} \right.$ , yielding 42·6 per cent. of acetyl on decomposition by

magnesia, while the tetracetyl-acid would require 51, and the triacetyl-acid 43·5 per cent. Nachbaur also found that benzoyl chloride gave a dibenzoyl acid; but Schiff finds that it is a *tribenzoyl compound*. Neither the triacetyl- nor the tribenzoyl-gallic acid gives any coloration with ferric chloride; hence no phenol-hydroxyl is present in these compounds.

An aqueous solution of gallic ether with excess of lead acetate, gives a precipitate of the composition  $\text{C}_7\text{H}_2(\text{C}_2\text{H}_5)\text{O}_6 \left\{ \text{C}_7\text{H}_2 \text{C}_2\text{H}_5 \text{O}_5 \right\} \text{Pb}''_3$ ; when treated with ethyl iodide, this product formed much lead iodide, but nothing suitable for analysis was obtained.

Gallic ether, boiled with acetyl chloride for some hours, forms *tri-acetyl-gallic ether*; after eight months' standing, the oily product began to crystallise: it was insoluble in water but soluble in alcohol, and gave neither iron reaction nor lead precipitate. From the above facts,

the author assigns to gallic acid the formula  $C_6H_2 \begin{cases} CO.OH \\ OH \\ OH \\ OH \end{cases}$ .

On dry distillation at  $200^\circ$ — $250^\circ$ , gallic ether yields alcohol, and pyrogallic acid, and a little rufigallic acid as sublimates; a carbonaceous residue containing gallohumic acid,  $C_6H_3 \begin{cases} OH \\ O \end{cases}$ , is left.

C. R. A. W.

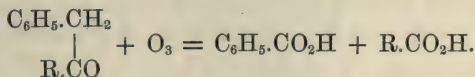
**Camphic Acid.** By BERTHELOT (Bull. Soc. Chim. de Paris [2], xvii, 390).

CAMPIC acid is a resinous product of the action of potash on ordinary camphor (*Ann. Chim. Phys.* [3], lvi, 94; *Ann. Chem. Pharm.*, cxlvi, 84; *ibid.*, clxii, 271, 419). Kachler has lately denied its existence, owing probably to his having boiled the material in an open cohobator for 250 hours, while the author operated in sealed tubes at  $180^\circ$  for 8 to 10 hours. Yet Kachler himself, as his memoir indicates, really obtained camphic acid as his principal product.

C. G. S.

**Oxidation-products of the Benzyl-ketones.** By A. POPOFF (*Deut. Chem. Ges. Ber.*, v, 500).

ON *à priori* grounds it was to be expected that the oxidation of these ketones would take place in accordance with the following general equation, in which R denotes a primary alcohol-radical of the fatty series:—



Experiment shows that such is really the case. Thus benzylmethylketone,  $CO \begin{cases} CH_2.C_6H_5 \\ CH_3 \end{cases}$ , is oxidised to benzoic and acetic acids; benzylethylketone,  $CO \begin{cases} CH_2.C_6H_5 \\ C_2H_5 \end{cases}$ , to benzoic and propionic acids.

These two ketones were prepared by the action of zinc methide and ethide respectively on phenylacetic chloride,  $C_6H_5.CH_2.COCl$ , obtained by the action of phosphorus pentachloride on phenylacetic acid from benzyl cyanide. The yield of chloride is very unsatisfactory, not exceeding ten per cent. The methylketone boils at  $214^\circ$ — $216^\circ$ , and forms a crystalline compound with sodium-hydrogen sulphite; the ethylketone boils at  $225^\circ$ — $226^\circ$ , but does not combine with acid sulphites.

H. E. A.



**On the Formation of Aniline Red, and on the Isomeric Toluidines.** By A. ROSENSTIEHL (Ann. Chim. Phys. [4], xxvi, 189—254).

THE commercial liquid toluidine operated upon by the author was a coloured oil which, when dry, boiled steadily at  $178^{\circ}$ . When it was cooled to near zero, the introduction of a crystal of toluidine caused the deposition of so large a quantity of crystalline matter, that the mass becomes semi-solid. The crystalline portion, freed from the liquid by pressure, is the toluidine of Hofmann and Muspratt. The portion of the alkaloid remaining liquid after exposure to cold, still contained toluidine; it was converted into oxalate, and the oxalate treated with ether in an automatic displacement apparatus.

The oxalate of ordinary toluidine was in this way left behind, whilst the ether dissolved out the salt of a base which, after drying over fused potash, boiled at  $198^{\circ}$ , and on analysis gave numbers agreeing with those required by the formula of toluidine. Hence common liquid toluidine is a mixture of at least two isomeric alkaloids having the same boiling point, but differing in melting point and in the solubility of their oxalates. The author ascertained by special experiments that the existence of the isomeric toluidines in the mixture was not due to the transformation of one of them under the influence of the heat employed in the operations to which they were subjected; the differences originate in the nitrotoluene from which the bases were prepared.

Before studying the properties of the liquid which the author calls *pseudotoluidine*, a portion of the oxalate which had been dissolved out by ether, was converted into hydrochloride and fractionally crystallised.

Three successive deposits were obtained which had the same crystalline form and solubility: the homogeneity of the product was thus ensured.

Pure pseudotoluidine is a colourless liquid, possessing the oily consistence of aniline, and powerfully refractive, but without action on polarised light. It does not solidify at  $-20^{\circ}$ . Boiling point  $202^{\circ}$  (corrected) under a pressure of 741 mm. If not perfectly dry, the boiling point is four or five degrees lower: Density at  $16.3^{\circ} = 1.002$ .

100 parts of water at  $28^{\circ}$  dissolve 1.6 of pseudotoluidine.

"	"	at $45^{\circ}$	"	1.7	"
"	"	at $22^{\circ}$	"	3.2	of aniline.

Pseudotoluidine resembles aniline in general chemical properties more nearly than toluidine. It appears to be a more feeble base than toluidine, as that body is capable of partly displacing it from its salts.

The salts of pseudotoluidine are colourless when prepared from the recently distilled alkaloid, but when the latter has become brown by exposure to the air, the addition of an acid developes a violet-red colour which is often very intense.

The same red colour, which is due to the formation of a small quantity of pseudorosanine, is developed when a salt of the new base is exposed to air and light. By this reaction very minute quantities of pseudotoluidine may be detected.

Pseudotoluidine, since its discovery, has been produced by several processes. Hübner and Wallach (*Zeit. f. Chem.*, v, 139) and Körner (*Compt. rend.*, 5 April, 1869) obtained almost simultaneously a base presenting all the characters of pseudotoluidine by nitrating and then reducing crystalline bromotoluene, and afterwards replacing the bromine by hydrogen by the action of sodium amalgam.

Nearly at the same time Beilstein and Kuhlberg effected an analogous metamorphosis by operating upon crystalline nitrotoluene. By nitrating and amidating that body, they obtained a nitrotoluidine from which they removed the group  $\text{NH}_2$  by Griess's method. They thus obtained a liquid nitrotoluene which furnished by reduction an alkaloid having all the characters of pseudotoluidine.

The author has also found that pseudotoluidine is produced in small quantity by the reduction of amidodracylic and anthranilic acids, by means of hydriodic acid, or by the action of heat upon the same bodies; also that it exists in the aniline obtained from indigo. Lastly, pseudotoluidine is formed, according to Beilstein and Kuhlberg, by the distillation of para-amidotoluic acid with soda-lime.

The question of the constitution of the toluidines has been studied by several chemists besides the author. According to Körner, pseudotoluidine corresponds to amido-benzoic acid; according to the author, to amido-dracylic or to anthranilic acid; according to Beilstein and Kuhlberg, to anthranilic acid.

For purposes of comparison, the author prepared quantities of chemically pure aniline and toluidine; the former by preparing the oxalate from the commercial substance and dissolving out the pseudotoluidine salt by means of ether. Pure toluidine is more difficult to obtain. For this purpose he employed the oxalate insoluble in ether, which formed the residue left after the extraction of pseudotoluidine.

The true melting point of toluidine was found to be  $45^\circ$ .

The salts of pure toluidine do not become red in the air, but assume only a yellow tint. The red coloration is due to the presence of pseudotoluidine.

Toluidine was discovered by Hofmann and Muspratt among the products of the reduction of crude nitrotoluene, and its formation has since been shown to be due to the presence of the crystalline nitrotoluene. The author has also obtained a mixture of toluidine and pseudotoluidine by nitrating crude bromotoluene, amidating the resulting mixture of nitro-bromo-toluenes, and then replacing the bromine by hydrogen. Assuming that the pseudotoluidine is derived from the crystalline bromotoluene, toluidine is probably formed from a liquid isomeric bromotoluene.

The author has also established the fact that toluidine is formed by the reducing action of hydriodic acid upon nitrobenzoic acid, and the base obtained by this process is free from aniline and pseudotoluidine when the nitrobenzoic acid is pure.

The author has made a detailed examination of the crystalline form, solubility and other physical characters as well as chemical composition of many of the salts of pseudotoluidine.

The hydrochloride is chiefly remarkable for the facility with which its solutions become supersaturated, and the author bases upon this



peculiarity a process for the manufacture of pseudotoluidine on a large scale. The commercial liquid alkaloïd is first exposed to a low temperature, so as to separate the greater part of the toluidine, and is then saturated with strong hydrochloric acid. The solution left to cool, slowly assumes a condition of supersaturation, and crystallisation of one or other of the bases may be determined by dropping into it a crystal of either of the hydrochlorides.

The neutral sulphate of pseudotoluidine contains  $2\text{H}_2\text{O}$ , whilst the corresponding salt of toluidine is anhydrous. The platino-chloride is very unstable. The nitrate, the oxalates, and the formate, pseudoformtoluide and pseudo-oxatoluide, have also been examined (for the Oxalates, see this Journal, p. 248).

For the preparation of large quantities of pseudotoluidine, the author recommends three processes, of which the first, based upon the production of supersaturated solutions of the pseudotoluidine hydrochloride has just been described. In the second process, advantage is taken of the difference of solubility of the acid oxalates, the toluidine salt being soluble only to the extent of 1 in 125 parts of water. The third method consists in the fractional saturation of the mixture of the two toluidines by an acid, preferably sulphuric. In such a mixture the toluidine enters into combination first, and the free pseudotoluidine may then be volatilised with the vapour of water.

*Reactions of Aniline, Toluidine, and Pseudotoluidine.*—All three alkaloids, produce with oxidising agents, coloured reactions, which admit of classification into two divisions according to the colour which they produce. The first division includes oxygen and chlorine, and bodies which act like them, such as the chromates, permanganates, chlorates, hypochlorites, peroxides of manganese and lead, and under certain conditions a mixture of hydrochloric and nitric acids. The second division comprises nitric acid, and mixtures in which it is generated.

Aniline dissolved in concentrated sulphuric acid and treated with the oxydants of the first class, gives a fine blue coloration, which disappears on dilution either by exposure to the air, or by addition of water.

Pseudotoluidine with the same gives a blue coloration which on dilution passes into violet-red.

With nitric acid, pseudotoluidine becomes coloured orange, and afterwards brown, if the solution is very concentrated. On the addition of water, the yellow colour is redeveloped.

Toluidine gives under all these circumstances reactions which are the inverse of those produced by the other two bases. Thus with oxydants of the first type, a yellow coloration only is produced, but with nitric acid toluidine produces a fine blue colour, the intensity of which is so great, that its production may serve for the detection of minute quantities of nitrates even when mixed with a large proportion of chloride. When the reaction is employed for this purpose, it is necessary that the sulphuric acid employed possess as nearly as possible the composition  $\text{SO}_4\text{H}_2\cdot\text{H}_2\text{O}$ : a little more water or acid renders the reaction less definite.

According to the author, the various colour tests which have been



indicated as characteristic of aniline, are with one exception due to foreign substances, and do not in reality belong to aniline. The exception is the reaction with hypochlorites discovered by Runge. The fugitive character of the colour is due not, as hitherto supposed, to the instability of the blue compound, but to the formation of brown insoluble matters which mask the colour, but are soluble in ether. Hence, when equal volumes of ether and water containing a trace of aniline are agitated with a few drops of solution of chloride of lime, and the mixture is allowed to separate, the ether assumes a red-brown colour, whilst the watery solution presents a pure blue.

When pseudotoluidine is submitted to the same treatment, the water is coloured yellow, then brown. If the ethereal solution is then separated and agitated with water acidulated with sulphuric acid, a magnificent violet-red solution is obtained, which resembles a solution of permanganate. Aniline under the same condition produces no colour but simply a slight greenish-black precipitate, and toluidine treated by water, ether, and chloride of lime, undergoes no visible change.

*Analysis of Mixtures containing Two of the Bases.*—To detect small quantities of aniline in pseudotoluidine, about 2 decigrams are dissolved in 80 grams of pure ether, and sufficient oxalic acid is then added to convert the bases into acid oxalates. The oxalate of aniline being least soluble, is deposited in small crystals, which may be further examined by appropriate colour tests.

To discover traces of pseudotoluidine in aniline, the mixture is treated with water, ether, and chloride of lime, and the pseudotoluidine sought for in the ethereal layer.

To detect traces of aniline in presence of toluidine, the chloride of lime test with ether may be employed advantageously.

It is not so easy to find small quantities of toluidine in aniline. A sulphuric acid solution of the two alkaloids is coloured crimson by nitric acid so long as the proportion of toluidine exceeds 10 per cent., but when the proportion is smaller, recourse must be had in the first place to fractional precipitation.

A mixture of toluidine and pseudotoluidine is best examined by the quantitative method already described in this Journal, p. 248.

*Action of Various Oxidising Agents, employed industrially, upon Aniline, Pseudotoluidine and Toluidine.*—A mixture of the hydrochloride of the base with a chlorate and a copper salt printed upon calico gave the following results :—

Aniline, very dark green.

Pseudotoluidine, very dark blue green.

Toluidine, bright maroon.

After immersion in a hot weak solution of carbonate of sodium, the shades had undergone the following modifications :—

Aniline, very deep blue-black.

Pseudotoluidine, very deep violet-black.

Toluidine, brown without lustre.

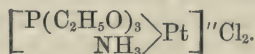
*Appendix.*—Commercial xylydine, like the xylene from which it is prepared, is a mixture of several isomerides. After conversion into

hydrochloride, it gave two different kinds of crystals, which were easy to pick out from each other. The alkaloïds separated from these crystals distil between  $210^{\circ}$  and  $214^{\circ}$ , and present the same reactions. In sulphuric acid solution with nitric acid, they give a blue coloration which changes to violet, red, and orange. The aqueous solution with ether and chloride of lime, gives no coloration. So far, xyloidine resembles toluidine, but it differs from that body in the fact that its ethereal solution is not precipitated by oxalic acid. These results are mentioned because had xyloidine been present in the bases studied by the author, it might have been passed without detection.

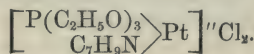
W. A. T.

**Phosphoplatinic Compounds containing Toluidine.** By G. SAILLARD (Compt. rend., xxiv, 1526).

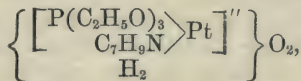
THE author extends Schützenberger's recent researches on phosphoplatinic compounds. That chemist, having formed the substance  $\text{P}(\text{C}_2\text{H}_5\text{O})_3\text{PtCl}_2$ , treated it with alcohol, and obtained an ether, having the formula  $\text{P}(\text{C}_2\text{H}_5\text{O})_3\text{Cl}_2$ , which in the presence of ammonia, yielded the derivative—



The author has obtained a compound, in which the ammonia of the last-named body is replaced by toluidine, by heating an alcoholic solution of the ether  $\text{P}(\text{C}_2\text{H}_5\text{O})_3\text{Cl}_2$  with excess of crystallised toluidine. It appears in the form of prismatic colourless needles, very slightly soluble in water or ether, soluble in alcohol, having the formula—



On treating this compound with potash,  $2\text{Cl}$  are replaced by  $2\text{HO}$ , forming the body—



which crystallises in fine silky needles, insoluble in water.

B. J. G.

**Colouring Matters derived from the Aromatic Azodiamines**  
**II. Safranine.** By A. W. HOFMANN and A. GEYGER (Deut. Chem. Ges. Ber., v, 526—533).

THIS fine red dye is met with in commerce under the form of a paste, and of a yellowish-red powder which contains the hydrochloride of the base mixed with calcium carbonate and common salt. On boiling this with water and allowing the solution to cool, a crystalline substance separates, which, after repeated recrystallisation from water, will be found to leave no residue when burnt. It however loses hydrochloric acid by these operations and becomes more soluble, so that

the addition of hydrochloric acid to the mother-liquors causes a further separation of the crystalline hydrochloride.

*Safranine Hydrochloride*,  $C_{21}H_{20}N_4.HCl$ .—In order to obtain the normal hydrochloride, it is necessary to acidify the boiling solution of the salt with hydrochloric acid. It forms thin crystals of a reddish colour, which are soluble in water and in alcohol, especially when heated. It is insoluble in ether and in a concentrated solution of salt. Both the aqueous and alcoholic solutions have an intensely yellowish-red tint. The addition of ether to the latter solution causes the precipitation of the hydrochloride.

*Safranine Platinochloride*,  $2(C_{21}H_{20}N_4.HCl).PtCl_4$ .—Obtained by precipitating a warm solution of the hydrochloride with excess of platinum chloride, and washing the precipitate with dilute hydrochloric acid. It is a crystalline yellowish-red powder, almost insoluble in water, alcohol, and ether.

*Safranine*.—Owing to the ready solubility of the free base in water, it is necessary to decompose the solution of the hydrochloride by silver oxide, and evaporate the deep red liquid thus obtained. On cooling, red brown crystals are deposited, which closely resemble the hydrochloride in appearance, but, as the solution retains silver chloride, it was not possible to obtain the base sufficiently pure for analysis. It dissolves easily in water and in alcohol. Dried at  $100^\circ$ , it acquires a feeble, greenish, metallic lustre. The addition of hydrochloric acid to the aqueous solution of the base again precipitates safranine hydrochloride.

*Safranine Nitrate*,  $C_{21}H_{20}N_4.HNO_3$ .—On adding an excess of dilute nitric acid to a hot aqueous solution of the free base, and allowing the liquid to cool, the nitrate separates in fine red-brown needles, which are difficultly soluble in cold, but readily in hot water. It is decidedly less soluble than the hydrochloride.

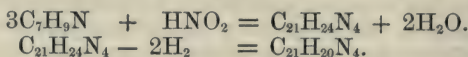
*Safranine Picrate*,  $C_{21}H_{20}N_4.C_6H_3(NO_2)_3O$ .—When picric acid is added to a dilute solution of safranine hydrochloride, or nitrate, the picrate is precipitated in brownish-red needles which are insoluble in water, alcohol, or ether.

*Safranine Hydrobromide* is precipitated in microscopic needles on adding hydrobromic acid to a solution of the base. It is almost insoluble in cold, but soluble in boiling water. The addition of bromine to a solution of the hydrochloride causes a precipitate which, when recrystallised from water, yields needles having a metallic green lustre. The *hydriodide* is similar to the hydrobromide. *Safranine sulphate* is a moderately soluble salt, precipitated by the addition of sulphuric acid to a concentrated solution of the base. On warming the liquid, it redissolves, and separates again in fine needles on cooling. The *oxalate* is very similar, but somewhat less soluble. The *acetate* is very soluble.

The most characteristic reaction of safranine is that when strong hydrochloric acid, or, better, sulphuric acid is gradually added to its solutions, the colour changes first to a fine violet, and then successively to blue, dark green, and light green. On diluting the solution, the same changes of colour are observed in reverse order. Safranine is prepared commercially by treating aniline of high boiling point succes-



sively with nitrous acid and arsenic acid, but the authors, in their experiments, found it better to employ chromic acid as the oxidising agent; the yield, however, is very small. Neither pure aniline, nor solid toluidine, nor a mixture of the two, yields safranine, although it can be obtained from pure liquid toluidine boiling at  $198^{\circ}$ . Safranine therefore, seems to be undoubtedly a toluidine derivative.



From a comparison of the formulæ of safranine,  $\text{C}_{21}\text{H}_{20}\text{N}_4$ , and mauveine,  $\text{C}_{27}\text{H}_{24}\text{N}_4$ ,\* it would appear probable that the latter is phenylated safranine,  $\text{C}_{21}\text{H}_{19}(\text{C}_6\text{H}_5)\text{N}_4$ . In fact safranine when treated with aniline yields a purple dye, and mauveine and safranine give similar colour reactions with sulphuric acid; moreover, Mr. Perkin has noticed that a substance resembling safranine occurs as a bye-product in the preparation of mauveine. The authors intend to investigate this subject.

C. E. G.

### The Alkaloids of *Sabadilla* Seeds. By F. WEIGELIN (Chem. Centr., 1872, 229).

THE pounded seeds, freed from their capsules, are boiled with very dilute sulphuric acid, and the extract is treated with three times its volume of 80 per cent. alcohol to precipitate mucilaginous matters; after evaporation of the alcohol, the boiling solution is precipitated by ammonia, whereby a resinous mass is obtained containing *veratrine*, which may be purified by solution in ether, evaporation, solution of residue in alcohol, and repeated precipitation by water. The ammoniacal filtrate is agitated with amylic alcohol, the extract evaporated, the residue dissolved in alcohol, and precipitated with water, and the precipitate purified by animal charcoal: finally, the concentrated solution of the bases is precipitated by ammonia. Ether extracts from the precipitate a bright-red substance, *sabatrine*,  $\text{C}_{51}\text{H}_{86}\text{N}_2\text{O}_{17}$ , and leaves behind *sabadilline*,  $\text{C}_{41}\text{H}_{66}\text{N}_2\text{O}_{13}$ , to be purified by solution in boiling water. The latter alkaloid is not absolutely insoluble in ether, and is not carbonized by sulphuric acid, but gives a yellow solution, becoming blood-red, and, finally, carmine-coloured: ammonia does not precipitate it from its salts, and alkaline carbonates only give a turbidity with boiling concentrated solutions (1 to 5). It is soluble in benzene, amylic alcohol, petroleum spirit, and chloroform, and is crystallisable from benzene, but not from water or alcohol; it neither produces sneezing, nor emetic action in frogs, but accelerates the action of the heart. Its gold salt,  $\text{C}_{41}\text{H}_{66}\text{N}_2\text{O}_{13} \cdot 2\text{HCl} \cdot \text{Au}_2\text{Cl}_6$ , is amorphous; its hydrochloride and sulphate are gummy.

Sabatrine much resembles sabadilline in properties; it gives two compounds with gold chloride, the one amorphous =  $\text{C}_{51}\text{H}_{86}\text{N}_2\text{O}_7 \cdot 2\text{HCl} \cdot \text{Au}_2\text{Cl}_6$ , the other crystalline, =  $5(\text{C}_{51}\text{H}_{86}\text{N}_2\text{O}_7 \cdot 2\text{HCl}) \cdot 11\text{Au}_2\text{Cl}_6$ .

\* According to Perkin's latest researches, the formula of mauveine is  $\text{C}_{26}\text{H}_{24}\text{N}_4$ . —ED.

Veratrine can be obtained in two modifications, one of which is readily soluble in water: its formula is  $C_{52}H_{86}N_2O_{15}$ , the author finding much less nitrogen than preceding chemists.

C. R. A. W.

### Compounds of Alkaloids with Bile-acids. By

W. F. DE L'ARLRE (Chem. Centr., 1872, 231).

THE gall of oxen, pigs, and dogs, and the sodium salts of glyco-, hyoglyco-, and tauro-cholic acids, give crystalline precipitates with some alkaloids, amorphous with others: the precipitates usually contain excess of acid, and are decomposed by diffusion, and dissolved by hydrochloric acid, re-appearing on neutralisation; excess of bile or bile-acids also dissolves them. The salts of strychnine, brucine, quinine, cinchonine, veratrine, emetine, and quinidine give difficultly soluble compounds, while those of morphine, nicotine, and conine are easily soluble: the strychnine and quinine compounds are about as energetic physiologically as the nitrate and hydrochloride of these bases respectively.

C. R. A. W.

### Muscarine, a Vegetable Base contained in *Agaricus Muscarius*.

By C. RUCKERT (N. Rep. Pharm., xxi., 193—208).

SCHMIEDBERG obtained this alkaloïd by treatment of the evaporated juice with alcohol, precipitation of the solution with lead acetate (after removal of alcohol by evaporation), and extraction with alcohol, and finally with ether, of the residue left on evaporation of the filtrate to dryness, and addition of sulphuric acid; the crude sulphate thus obtained was precipitated by mercury-potassium iodide, and the washed precipitate decomposed by sulphhydrate of barium, prepared by adding barium hydrate and passing sulphuretted hydrogen into the mixture. The author finds that this process yields about 0.7 to 0.8 grm. of muscarine sulphate from 1 kilogram of thick extract.

Muscarine forms a colourless syrupy substance, without taste or smell, soluble in all proportions of water and alcohol, insoluble in ether, and only sparingly soluble in chloroform; it becomes crystalline over sulphuric acid, but is very deliquescent. It has a strong alkaline reaction, and precipitates iron and copper salts; boiling for 5—10 minutes with potash-ley or diluted sulphuric acid has no apparent action on it; heated with moist solid potash, it evolves ammoniacal vapours of a fishy odour, no browning taking place until the heat has been continued for some time. Manganese dioxide and sulphuric acid, chlorine-water, permanganate of potassium, potassium chromate and sulphuric acid, produce no coloration, the oxidizing agents being, however, reduced. Excess of bromine-water gives a yellow precipitate, soon re-dissolving, and forming a yellow solution, which soon becomes colourless.

Mercury-potassium iodide and bismuth-potassium iodide give amorphous precipitates, becoming crystalline on standing; gold chloride yields a non-crystalline precipitate, while mercury chloride yields crystals on long standing; platinum chloride, potassium ferrocyanide,

and platinocyanide and tannin do not precipitate the sulphate, which is a deliquescent salt, becoming crystalline over sulphuric acid. No analytical numbers are given. The physiological action of muscarine is antagonistic to that of atropine.

C. R. A. W.

**Oxidation of Conglutin from Lupines by Potassium Permanganate.** By R. POTT (J. pr. Chem. [2], v., 355—365).

CONGLUTIN, purified by two precipitations, was dissolved in potash solution, and treated with potassium permanganate in proportions varying from a quarter part to six parts of the latter to one of the former, the whole being frequently agitated without application of heat. At the end of an interval varying from 1 to 11 days, a colourless solution could be filtered from the manganese hydrate; this was evaporated on the water-bath, with addition of sulphuric acid, to neutralise the potash; butyric acid was evolved, and a precipitate of a substance like casein formed in some cases, but not in all. After filtration and distillation, alcohol was added to the residue, to throw down potassium sulphate, and then barium carbonate, whereby a soluble salt was obtained, precipitable by alcohol. From the barium salt thus purified by several precipitations, a syrupy acid was obtainable by means of sulphuric acid and evaporation; the alcoholic filtrate from the barium salt gave a syrupy mass on evaporation. On analysis the following results were obtained:—

	Carbon.	Hydrogen.	Nitrogen.	Oxygen.
Casein-like precipitate . . . }	49·40 to 50·32	6·15 to 7·32	16·07 to 16·12	27·62 to 27·67
Acid from barium salt .. }	37·63 to 38·23	5·83 to 6·06	10·68 to 11·34	45·03 to 45·20
Syrupy mass . . .	36·67 to 42·68	6·04 to 6·99	12·36 to 15·51	37·84 to 43·45

The barium salt itself gave these numbers—

Carbon.	Hydrogen.	Barium.	Nitrogen.
21·68 to 25·78	2·17 to 3·33	32·62 to 39·94	4·11 to 6·29

By precipitation with lead acetate, a lead salt of the nitrogenous acid was obtained after decomposition by sulphuretted hydrogen; this yielded a syrupy acid containing

Carbon.	Hydrogen.	Nitrogen.	Oxygen.
45·44 to 45·53	5·84 to 5·88	13·06 to 13·31	35·32 to 35·62

C. R. A. W.



## Physiological Chemistry.

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**Experimental Researches on the Influence of Changes in the Barometric Pressure on the Phenomena of Life.** By P. BERT (Compt. rend., lxxiii, 213, 503; lxxiv, 617; lxxv, 29, 88).

THE author finds that at pressures under 18 centimeters of mercury animals die from want of oxygen; at pressures of one to two atmospheres, from want of oxygen and presence of carbonic acid; at 2—6 atmospheres, from the presence of carbonic acid alone; at 6—15 atm., from the presence of carbonic acid and of excess of oxygen; and at 15—25 atm., from the poisonous action of oxygen alone. Animals die from want of oxygen when the amount contained in their arterial blood is not sufficient to balance a pressure of 3·5 per cent. of oxygen in the atmosphere. They die from poisoning by carbonic anhydride when the amount contained in their venous blood is sufficient to balance a pressure of 26 to 28 per cent. of carbonic anhydride in the atmosphere in the case of sparrows, of 28 to 30 for mammals, and of 15 or 16 for reptiles.

As the pressure of oxygen in the surrounding air depends on two factors, the percentage proportion and the barometric pressure, the barometric pressure may be reduced to 6 centimeters for sparrows if the proportion of oxygen in the air is increased, and it may be raised to 23 atmospheres without causing death, if the proportion of oxygen is reduced by mixing the air with nitrogen. Aeronauts might therefore ascend higher than it has hitherto been possible to do, by taking with them a bag of oxygen to inhale; and the danger which threatens divers of being poisoned by the oxygen in the compressed air might be averted by using a mixture of air and nitrogen.

From an examination of the gases in the blood of animals confined in rarefied air, the author finds that both the oxygen and carbonic anhydride in the blood diminish. The dyspnoea which is felt in ascending mountains is therefore due to want of oxygen in the blood. The diminution in oxygen becomes diminished at 20 centimeters pressure; yet this is the pressure under which the inhabitants of the elevated Mexican plateau of Anahuac live. The oxygen diminishes more quickly and more regularly than the carbonic anhydride. Although there are but very small quantities of gases simply dissolved in the blood, the chemical combinations in which they take part are dissociated very easily and in a progressive manner under the influence of diminished pressure, and this dissociation takes place more easily in the organism than in experiments *in vacuo*.

T. L. B.

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**The Inorganic Constituents of the Blood.** By A. JARISCH (Ann. Chem. Pharm., clxiii, 236—247).

JARISCH has made (in Stricker's laboratory at Vienna) analyses of the inorganic constituents of dogs' blood with more than ordinary care and precautions. The blood was received direct from the vessel in

carefully weighed and stoppered flasks surrounded by ice in order to avoid loss by evaporation. The weight was accurately determined after the blood had been allowed to thaw. The blood was then carefully evaporated, and the mass, before complete incineration, digested with hot water in order to extract soluble chlorides, &c., and thus provide against loss of these constituents by strong heat. The solution was evaporated, incinerated to destroy organic matters, and redissolved in water. This solution was added to the fully incinerated mass, and the whole evaporated and dried. In this manner the inorganic constituents were obtained without loss. As, however, even after the most careful incineration, it is almost impossible to get rid of all the carbon, the results are always a little too high, but serious error is eliminated by comparison of the found with the calculated constituents.

The ash so obtained is partly soluble in water, and completely so in hydrochloric acid. The watery solution has an alkaline reaction. The alkaline reaction is neutralised by a drop or two of dilute acid, and the ash probably consists of neutral salts and iron oxide. The method of quantitative determination is fully given in the original paper.

Tables are given of the results of four analyses, three of arterial and one of venous blood. The percentage amounts are compared with those given by Verdeil. There is a general agreement in many points, but Jarisch finds no carbonic acid, and his percentages of soda and potash differ considerably from those given by Verdeil. The following is the mean percentage of the various constituents calculated from four analyses:—

Phosphoric anhydride .....	0·1103
Sulphuric anhydride .....	0·0358
Chlorine .....	0·2805
Potash .....	0·0342
Soda .....	0·3748
Lime .....	0·0112
Magnesia .....	0·0058
Iron oxide.....	0·0948
Calculated total, 0·8640; found, 0·8922	

D. F.

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**Iron in the Blood and in Food.** By M. BOUSSINGAULT (Compt. rend., lxxiv, 1355—1359).

NUMEROUS analyses are given, showing the wide distribution of iron in articles of food and in the animal body. The quantity of iron taken daily by a man in his food and drink is estimated at from ·0591 to ·109 gram. Observations are offered on the existence of iron in the colouring matter of blood and of plants respectively. It is asserted that etiolated plants and the bodies of animals having white blood contain only as much iron as green plants and animals nourished with red blood.

T. S.

**Reaction of the Blood in Leukæmia.** By Prof. MOSLER  
(*Zeitsch. f. Biologie*, viii, 147—151).

In a case of well-marked leukæmia the author found that the blood presented an alkaline reaction when freshly drawn, and did not become acid for four days.

T. L. B.

**Formation of Urea in the Organism.** By O. SCHULTZEN and  
M. NENCKI (*Zeitsch. f. Biologie*, viii, 124—146).

It has been supposed by many chemists that albumin contains the complex of atoms of urea, and that the latter substance is a direct product of the gradual oxidation of the former. All attempts to produce urea by oxidation of albumin have failed, the products obtained by using oxidising agents being ammonia, benzoic acid, benzaldehyde, and aldehydes of the fatty series, while those got by the use of acids and alkalis are ammonia and amido-acids of the fatty and aromatic series (glycocine, leucine, and tyrosine). These three bodies, leucine, tyrosine, and glycocine, constantly occur in the animal body under normal conditions. Glycocine can be removed from the body in considerable quantities by the administration of benzoic acid, and leucine and tyrosine occur in pleuritic or ascitic exudations. Whenever albumin decomposes and oxidation is hindered by the absence of hæmoglobin, as is the case in pus, much leucine and tyrosine are found, but little or no urea; and when the oxidising power of the organism is diminished, as in acute atrophy of the liver and in phosphorus poisoning, much leucine and tyrosine occur in the urine, but scarcely any urea. These circumstances led the authors to believe that the amido-acids of the fatty series, and perhaps tyrosine, were the intermediate links between albumin and urea. In order to test this hypothesis, they fed dogs on a diet containing a constant but small amount of nitrogen, and thus got a constant and small amount of nitrogen in the urine. They then gave the animals a quantity of leucine, tyrosine, or glycocine in order to see if the amount of urea in the urine was increased, as it must be if these substances are transformed into it in the body. The result was, that after the administration of leucine or glycocine, the amount of urea in the urine was greatly increased and the nitrogen contained in the additional urea very nearly corresponded with that of the glycocine and leucine, clearly showing that these bodies are converted into urea. The urea was also increased by tyrosine, but not to so great an extent, and part of the tyrosine appeared unchanged in the urine and fæces. The authors therefore think that the greater part of the tyrosine is absorbed from the intestine, but is destroyed so slowly in the body that a part of it is excreted unchanged in the urine, while that portion which does undergo transformation is excreted as urea. When acetamide was given to the dogs, it was excreted unchanged, and no part of it was converted into urea. As amido-compounds analogous to acetamide are not excreted normally in the urine, the authors think that they are not formed during the decomposition of albumin in the body. Since amido-acids contain only one atom of nitrogen and urea contains



two, it must be formed from them by synthesis, and the authors think it likely that bodies from the cyanogen group form the intermediate links.

According to their idea, the albuminous substances contained in food take up water under the influence of the digestive ferments and are split up partly in the alimentary canal, but chiefly in the circulation, into amido-acids and non-nitrogenous bodies. The latter undergo combustion and yield carbonic acid and water, while the amido-acids form urea. They think it not improbable that ammonia is liberated from albumin simultaneously with cyanic acid, and unites with it to form urea, or with cyanogen to form cyanamide, which is then transformed into urea.

The urea in their experiments was determined by Bunsen's method, which the authors have improved. For details the original paper must be consulted. Liebig's method did not answer, as acetamide precipitated the mercuric nitrate as well as urea.

T. L. B.

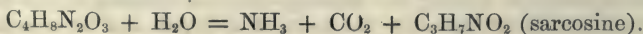
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**The Origin of Urea in Animal Bodies.** By O. SCHULTZEN  
(Dent. Chem. Ges. Ber., v, 578).

THE author's previous researches have indicated that many nitrogenous substances containing one atom of nitrogen (*e.g.*, leucine, glycocine, &c.) become changed into urea in animal bodies, the increase in urea being precisely equal to that due to the nitrogen in the leucine or glycocine administered; on attempting to obtain substituted ureas by means of feeding on substituted glycocines striking results were obtained.

Phenyl-glycocine was found to be too poisonous to be of service; but methyl-glycocine (sarcosine), when administered to a well-nourished dog in such quantities that the nitrogen thus furnished was equal to that excreted daily as urea, caused an entire absence of urea from the urine, its place being taken by a new compound,  $C_4H_8N_2O_3$ .

The urine voided within two hours after feeding was precipitated with basic lead acetate, the filtrate shaken with silver oxide to remove chlorine, and the filtrate treated with sulphuretted hydrogen, evaporated to a syrup, decomposed by sulphuric acid, and agitated with a large bulk of ether; on distillation the ether left a quantity of syrupy extract composed of two substances: the aqueous solution was boiled with barium carbonate whereby much carbonic acid was evolved, and the solution evaporated to dryness and treated with absolute alcohol; this left undissolved the barium salt of a sulpho-acid, but dissolved out the new compound, the constitution of which appears to be  $H_2N-CO-N \begin{cases} CH_3 \\ CH_2.CO_2H \end{cases}$  or urea in which  $H_2$  is replaced by  $CH_3$  and acetic acid minus  $H$ , or what is the same, sarcosine in which  $H$  is replaced by the carbamide residue,  $CO.NH_2$ ; for on heating with baryta-water in a sealed tube, the substance undergoes the reaction—



The sulpho-acid above mentioned has the formula,  $\text{H}_2\text{N}-\text{SO}_2-\text{N} \begin{cases} \text{CH}_3 \\ \text{CH}_2.\text{CO}_2\text{H} \end{cases}$  the barium salt being  $(\text{C}_3\text{H}_2\text{N}_2\text{SO}_4)_2\text{Ba} + 2\text{H}_2\text{O}$ ; on heating this with excess of baryta-water, it forms barium sulphate, ammonia, and sarcosine. Other substances not yet fully investigated are also found in the sulphuric acid solution after treatment with ether.

Fowls fed with large quantities of sarcosine void urine containing no urea, new substances being formed instead; these and the other products are undergoing investigation, as well as the possible production of the compound  $\text{C}_4\text{H}_5\text{N}_2\text{O}_3$  by the action of cyanic ether on sarcosine.

C. R. A. W.

### Conversion of Bilirubin into Urinary Colouring Matter. By R. MALY (Ann. Chem. Pharm., clxiii, 77—95).

A PORTION of the results here detailed have already appeared in abstract (this volume, p. 514).

*Hydrobilirubin*, obtained by the action of sodium amalgam on bilirubin, is formed by the reaction—



It is a weak acid, forming soluble compounds with alkalis, lime, and magnesia, soluble or difficultly soluble ones with heavy metals; its solutions exhibit peculiar spectra somewhat modified by the state of concentration and the nature of the solvent (acid, alkaline), and exhibit a green fluorescence, this being most marked with an ammoniacal solution of the zinc or silver compound. Its relations to other analogous colouring matters are discussed at some length.

C. R. A. W.

### Formation of Hippuric Acid in the Urine of Herbivora. By HOFMEISTER (Versuchs-Stationen Organ, xiv, 458—470).

SHEEP fed on clover-hay secreted as an average 5.3 grams only of hippuric acid in 24 hours, but when fed on meadow-hay an almost constant quantity of 30 grams. The addition of benzoic acid to the clover-hay gave rise to an increase in hippuric acid of rather more than the calculated weight, showing that clover does not in itself prevent the formation. The distillate and watery extract obtained on distilling meadow-hay with water, dried and given to sheep, produced no increase in hippuric acid, but the dried residue caused its secretion in almost the same proportion as the original hay.

Meadow-hay was then exhausted consecutively with water, alcohol, and 3 per cent. soda-ley. The alcoholic extract produced a slight increase in hippuric acid; the watery and alkaline extracts and the residue had no appreciable effect. The non-formation of hippuric acid from this residue is in opposition to the observations of Meissner, who from experiments on rabbits arrived at the conclusion that the formation of this acid was due to the digestion of some substance contained in the crude fibre, probably the cuticular membrane. That the nitro-

genous constituents of the food do not wholly regulate the secretion of the acid is proved by the facts that the addition of rape-cake to the food had no action on its quantity, but only increases the urea, and that a much smaller quantity is formed by feeding with clover than with graminaceous plants.

Neither do the aromatic substances of the food seem to have much influence: for the alcoholic extract of meadow-hay, containing the greater part of the aromatic bodies, produced but a small quantity of hippuric acid, and Henneberg and Stohman found as much in the urine of oxen when fed on oat-straw as when eating meadow-hay.

By gradually increasing the quantity of oat-straw given in combination with clover-hay, the hippuric acid secretion in the urine of sheep was gradually increased; in a similar experiment with barley-straw no such increase took place.

Notwithstanding contradictory appearances, the author still thinks that the secretion of hippuric acid is influenced by the protein matters and the fibre of the food, though the conditions necessary can only be found by a closer examination of these substances. E. K.

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**Action of Crystallised Digitaline on the Temperature of the Body, and on Diuresis.** By MÉGEVAND and DAREMBERG (Bull. Soc. Chim. de Paris [2], xvii, 443).

CRYSTALLISED digitaline, recently obtained by M. Nativelle, is much more active than the most carefully prepared amorphous digitaline.

Mégevand submitted himself to experimentation. He lived on a uniform diet for five days; then, for three days, took with the same diet  $\frac{1}{2}$  milligram of the digitaline, and for the next three days  $\frac{1}{3}$  milligram; lastly, he lived on the same diet five days longer without any medication. Under the influence of this small dose the urea suffered a reduction of 30 per cent. and the quantity of the urine increased 25 per cent.; the pulse fell to 40 and the temperature of the body fell one degree. These modifications experienced their maximum of intensity on the two days following the ingestion of the medicament, which shows the cumulative property of this substance. Vomiting occurred on the sixth day.

E. D.

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**Respiration of the Larvæ of *Tenebrio molitor*.** By W. DETMER (Versuchs-Stationen Organ, xv, 196—201).

A GLASS vessel containing a known weight of meal-worms and wheat flour, had a constant stream of air drawn through it by means of a Bunsen's water-pump. The entering air was freed from carbonic acid, but supplied with moisture; the air leaving the chamber passed through the usual arrangement of potash-bulbs, &c. The chamber was kept dark. 14.489 grams of meal-worms, at a temperature of 12°—16°, yielded on an average .0566 grm. CO<sub>2</sub> in 24 hours; from this is to be deducted .011 grm. CO<sub>2</sub> due to the decomposition of the wheat-flour in moist air. The same meal-worms at a constant temperature of 22° gave .085 grm., and at a temperature of 35° .123 grm. CO<sub>2</sub> in 24 hours. The correction to be deducted for the oxidation of the flour



present amounted to .019 grm. at 30°. Meal-worms contain 42.15 per cent. of dry substance, and 6.44 per cent. of nitrogen. The author remarks that many of the difficulties of feeding experiments are due to the large size of the animals operated on. R. W.

**Animal Glycogenesis. Evolution of Glycogen in the Bird's Egg.** By CLAUDE BERNARD (Compt. rend., lxxv, 55—60).

A PHYSIOLOGICAL paper, relating to the above subject.

T. S.

**Influence of the Addition of Calcium Phosphate to the Food on the Composition of the Ash of Milk.** By H. WEISKE-PROSKAU (Ann. d. Landw. Wochen-Blatt, Sept. 6, 1871).

THE author experimented on two cows receiving a constant diet. The cows were supplied with precipitated calcium phosphate during 12 days in addition to their ordinary food. The milk was examined before, during, and after this phosphatic diet. The percentage composition of the milk exhibited no increase in ash, lime, or phosphoric acid during the supply of calcium phosphate; nor was there any increase in the absolute quantity of these substances yielded as milk. R. W.

**Chemistry of Vegetable Physiology and Agriculture.**

**Soil Statics and Soil Analyses (Part II).** By HERMANN V. LIEBIG (Zeitschr. d. Landw. Vereines, 1872).

THE author's analyses of the first 9 inches of surface soil from Mr. Lawes' wheat field are already given (page 318 of this volume); the second and third 9 inches gave the following results. The soils were in all cases boiled for half an hour with four times their weight of dilute acetic acid, the clear solution decanted, and the residue thoroughly washed with boiling water.

*Soluble in Dilute Acetic Acid in second 9 inches of Soil.*

100 parts of soil contain	No. 3. Unma- nured.	No. 10 a. Ammonia salts.	No. 5 a. Cinereal manure.	No. 7 a. Cinereals and Ammonia.	No. 2. Farmyard manure.
Silicic acid .....	.080	.070	.074	.076	.080
Ferric oxide and alu- mina .....	.152	.184	.150	.140	.168
Lime .....	.377	.332	.580	.355	.576
Magnesia.....	.013	.019	.031	.022	.025
Potash.....	.018	.019	.022	.018	.026
Soda.....	.013	.015	.020	.011	.028
Sulphuric acid .....	.002	.005	.007	.007	.009
Phosphoric acid in nitric acid extract }	.047	.047	.058	.061	.065

*Soluble in Dilute Acetic Acid in third 9 inches of Soil.*

100 parts of soil contain	No. 3. Unma- nured.	No. 10 a. Ammonia salts.	No. 5 a. Cinereal manure.	No. 7 a. Cinereals and Ammonia.	No. 2. Farmyard. manure.
Potash.....	·011	—	·011	·011	—
Soda .....	·014	—	·005	·005	—
Sulphuric acid .....	·003	—	·005	·005	—
Phosphoric acid in nitric acid extract }	·043	·053	·042	·040	·044

About one-fourth of the accumulated phosphoric acid in plots 5a, 7a, and 2, is found in the second 9 inches of soil, none has apparently reached the third 9 inches; the distribution of the phosphoric acid is greatest in the case of farm-yard manure.

The available potash on plots 3 and 10a is greater in the second 9 inches than at the surface, a fact which seems to indicate that wheat draws its potash chiefly from the surface-soil. On the plots where potash has been applied, a small accumulation is in two cases apparent in the second 9 inches, but none in the third; the widest distribution of potash is with farm-yard manure.\* The very small amount of available potash which occurs in every case in the third 9 inches is clearly owing to the protection of the silicates from the action of the weather. The third 9 inches of plot 3 treated with dilute *nitric* acid yielded ·085 per cent. of potash; the subsoil, therefore, contained far more potash than that soluble in acetic acid. A considerable part of the potash supplied in manure is unaccounted for by the available potash found in the soil; the author thinks the remainder may have assumed a zeolitic form in the subsoil, but there is no direct evidence for this in his results. The sulphates soluble in acetic acid and hot water are pretty evenly distributed through the depth of the soil. Much more sulphuric acid was obtained by treatment with dilute nitric or hydrochloric acid; insoluble sulphates appear, therefore, to be present. The greater part of the sulphuric acid supplied in manure has passed below the third 9 inches.

The analyses by acetic acid show that the subsoil was very poor in cinereal plant-food. The tendency of rotation and of manuring, is to accumulate food in the surface-soil. The author believes that the poverty of the subsoil is the reason why some deeply rooted crops, as clover and roots, often fail when repeated at too short intervals on the same land.

R. W.

**The Condition of Phosphoric Acid in Soils.** By P. WAGNER  
(Jour. f. Landw. B., xix, h. 1; and Ann. d. Landw. Wochen-Blatt,  
June 28, 1871).

It is impossible to ascertain the condition in which phosphoric acid

\* The farmyard manure supplied about as much phosphoric acid as the cinereal manure, but a good deal more potash.

exists in soil by extracting the soil successively with water, carbonic acid water or acetic acid, and hydrochloric acid; for though alkaline phosphates are soluble in water, and alkaline-earthly phosphates in water containing carbonic or acetic acid, the phosphoric acid is no sooner brought into solution by these means than it is liable to be reabsorbed by the ferric oxide of the soil, or, in the case of an aqueous solution, precipitated by salts of calcium or magnesium; the results obtained throw, therefore, no light on the original condition of the phosphoric acid. The solubility of calcium phosphate in carbonic acid water depends moreover on the presence or absence of calcium carbonate; in the former case but little phosphate is dissolved, however much may be present (compare *Jour. Chem. Soc.* [2], iv, 313, 315). For the same reasons, the amount of phosphoric acid existing as ferric phosphate cannot be separately determined.

R. W.

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**Influence of Vegetal Mould on the Porosity of Soils.** By TH. SCHLÖSING (*Compt. rend.*, lxxiv, 1408—1411).

THE porosity of soils could not long be preserved if the mineral dust were not agglutinated into granules by some substance acting as a cement, such as vegetal mould, or clay coagulated by lime salts. The required proportion of the latter is ascertained by mixing known weights of levigated clay with sand or chalk, drying till the still moist mass crumbles in the fingers, and besprinkling it very gently for three or four days with water containing traces of a calcium salt. With proper quantities of clay, the soil preserves its character; in other cases it is softened, and becomes impermeable. For 100 parts of sand about 11 of clay were required, for chalk a slightly larger amount.

If instead of clay, soluble or insoluble humates be used, it will be found that one per cent. of humic acid with lime or alumina (or two per cent. if strongly dried, pounded, and granulated as before), will enable the earth to resist prolonged washing. On the contrary, four per cent. of calcium or aluminium humate kneaded with clay causes it to break up into granules with water. In light soils, therefore, vegetal mould, by means of its humates, consolidates their particles; in heavy ones, by its organic *débris*, it destroys their solidity and impenetrable character, in both cases maintaining for some time the porosity of the soil.

C. G. S.

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**Manuring with Powdered Phosphorite.** By DIETRICH (*Ann. d. Landw. Wochen-Blatt*, Nov. 1 and 8, 1871).

THE great deposit of phosphorite in the district of Lahn is found to be unsuited for the manufacture of superphosphate of high quality, the large amount of ferric oxide and alumina it contains causing the phosphate made soluble by acid to revert to an insoluble condition. The author advocates the application of such phosphorites in a state of fine powder without previous treatment with acid. The solubility of the phosphorite is very small. Water saturated with carbonic acid dissolved in 12 weeks the following grams of phosphoric acid per 100 litres.



Lahn-phosphorite, best quality, 2·55; a lower quality, 1·66; Baker guano, 12·00; bone-dust, 16·72; precipitated tricalcic phosphate, 27·52. Large quantities of phosphorite may, however, be applied for the same price as small quantities of superphosphate; the action of the weather will also soften the phosphorite considerably, and the solvent power of the organic acids of the soil is probably not unimportant. The author quotes successful field experiments with ground phosphorite, and recommends extensive trials of large dressings of finely ground phosphorite mixed with saw-dust, turf, or other organic compost.

R. W.

**Composition of some Food-stuffs.** By H. WEISKE-PROSKAU  
(Ann. d. Landw. Wochen-Blatt, Sept. 6, 1871).

THE author examined the rank herbage which grows in patches on meadow land where manure has fallen, and which cattle eat with reluctance. Compared with the surrounding herbage, it was found to contain twice as much nitrogen, and rather more woody fibre and ash. The ash was much richer in soda and magnesia, and also contained rather more potash and sulphuric acid.

The percentage composition of other food-stuffs examined was as under:—

	Buckwheat grain.			Vetches grain.			Hay.					Green oats and vetches.
	Ordinary.	Scotch.	Partarian.	Ordinary.	White.	Grey.	French rye-grass.	Sainfoin.	Hop- trefoil.	White clover.	Bokharian clover.	
Water.....	9·57	10·57	10·62	12·93	13·68	14·36	8·15	11·77	11·84	9·82	12·00	81·50
Albuminoids.....	10·75	10·69	11·19	27·50	27·81	29·06	7·31	15·44	17·78	17·00	14·03	3·39
Soluble carbo- hydrates and fat.....	61·39	61·10	53·58	47·80	48·03	46·72	42·46	36·24	37·69	44·90	31·55	6·61
Crude fibre.....	15·55	14·96	20·01	7·17	6·87	6·22	33·99	30·86	25·16	18·83	37·00	6·36
Ash.....	2·74	2·68	4·60	4·60	3·61	3·64	8·09	5·69	7·53	9·45	5·42	2·14

The hay examined was harvested at the commencement of blossoming.

R. W.

**Constituents of the Rhizomes of *Triticum repens*.** By H. LUDWIG and H. MÜLLER (Arch. Pharm. [2], cl, 132—147).

THE authors obtained from *Triticum repens*—1. A (fruit) sugar with a strong left-handed rotatory power. 2. A right-handed uncrystallisable sugar, separated from the former by precipitation with lime. 3. A gummy matter, with a rotatory power of  $-48\cdot2^\circ$ , which is not precipitated by lead acetate, reduces alkaline copper solution, and when treated with dilute sulphuric acid yields a left-handed sugar. It is separated with difficulty from the nitrogenous ingredients. 4. A sweet-tasting intermediate product between the gum and fruit sugar.

From a rather old extract, mammellated crystals of calcium lactate

were obtained. This was probably the substance taken by Pfaff for a new kind of sugar.

E. K.

## Analytical Chemistry.

**Application of Sulphuretted Hydrogen Reactions to Analyses in the Dry Way.** By J. LANDAUER (Deut. Chem. Ges. Ber., v, 406).

THIS can be effected by heating the borax bead in which the metallic salt is dissolved, with sodium thiosulphate; but this method has the disadvantage of not being applicable to volatile metals like arsenic and mercury, besides that the production of liver of sulphur causes uncertainty by colouring the bead. Instead, therefore, of proceeding in this way, it is better to heat the substance with the thiosulphate in a test-tube. If the water of crystallisation of the reagent has not been previously expelled, the tube must be held horizontally to prevent the water running back and breaking it.

The annexed table shows that nearly all metallic compounds may be thus identified by means of the sulphide reactions aided by those with the borax bead.

Metallic oxide.	With $S_2O_3Na_2$ .	Cold borax bead.	
		In oxidising flame.	In reducing flame.
Antimony oxide..	Red .....	Colourless.....	Grey to colourless.
Arsenious acid ..	Yellow .....	0.....	0.
Lead oxide .....	Black.....	Colourless.....	Grey to colourless.
Chromium oxide ..	Green .....	Yellowish-green ....	Emerald green.
	(Cr(OH) <sub>3</sub> )		
Iron oxide .....	Black.....	Yellow .....	Bottle green.
Gold oxide .....	Black..... {	Reduced without {	Reduced without being
		being dissolved.. {	dissolved.
Cadmium oxide ..	Yellow .....	Colourless.....	Grey to colourless.
Cobaltous oxide ..	Black.....	Blue .....	Blue.
Cuprous oxide ..	Black.....	Blue .....	Brownish-red(troubled)
Manganese oxide ..	Bright green..	Violet .....	Colourless.
	(Mn <sub>2</sub> OS)		
Molybdic acid ..	Brown .....	Colourless.....	Brown.
Nickelous oxide ..	Black.....	Reddish-brown ....	Grey to colourless.
Platinum oxide ..	Black..... {	Reduced without {	Reduced without being
		being dissolved .. {	dissolved.
Mercury oxide ..	Black.....	0.....	0.
Silver oxide.....	Black.....	Colourless.....	Grey to colourless.
Uranium oxide ..	Black.....	Yellow .....	Bottle-green.
Bismuth oxide ..	Black.....	Colourless.....	Grey to colourless.
Zinc oxide .....	White .....	Colourless.....	Grey to colourless.
Tin oxide .....	Brown .....	Colourless.....	Colourless.

E. D.

**Note on the Estimation of Sulphur in Pyrites.** By H. B. YARDLEY (Chem. News, xxv, 257).

THE author, fancying that a trifling loss of sulphur was entailed when pyrites was rapidly oxidised with nitric acid at a boiling heat, undertook a few experiments in order to satisfy himself upon the point.

The results of several analyses tend to show that when the oxidation is conducted at a temperature below 100°, the total weight of barium sulphate obtained is somewhat less than when a higher temperature is adopted, and that so far from ebullition being detrimental to the accuracy of the analysis, it favours the complete oxidation of the sulphur and very slightly raises the percentage. The author, however, prefers as a rule to operate at the temperature of a water-bath, to ignite the insoluble residue, and to calculate from the loss of weight the amount of unoxidised sulphur.

J. W.

**Analysis of Drinking Waters by a Titrated Soap Solution.** By Dr. GRÆGER (Chem. Centr., 1872, 152—153).

A CALCIUM chloride solution is made, containing 0.25 gram dry calcium chloride in 1,000 c.c. water. A solution of soap containing no free alkali is so made that 23 measures of a small burette produce a permanent lather when shaken with 40 c.c. of the calcium chloride solution. 40 c.c. of the water to be tested are shaken up with the soap solution, and the number of measures required to produce a permanent lather is read off.

This number expresses *natural hardness*, caused by lime and magnesia salts, influenced also by free carbonic acid in the water.

A second trial is made after lime has been precipitated. A portion is boiled to expel free carbonic acid, and after the precipitated calcium carbonate has been filtered off, a third titration is effected. From 40—60 c.c. of the boiled water, all the lime is removed by precipitation, and a titration with soap-solution made, which gives magnesia only. The sulphuric acid and chlorine are estimated by adding to a known portion of the boiled water an exactly measured quantity of a nitrate of barium solution tested against the soap solution, then filtering, and titrating the filtrate with soap solution.

This process has been objected to, and the author examines these objections.

The magnesia estimation must be made in very dilute solution, or the results are too high. He admits that errors may occur when mixtures of many salts are present, especially in the estimation of *natural hardness*, but generally the results are consonant with those obtained by a gravimetric analysis.

M. M. P. M.

**Estimation of Reduced Phosphates.** By J. KÖNIG (Annalen der Landwirthschaft, 1871, 177—183).

THE same results as given before (*Zeitschr. f. Anal. Chem.*, x, 305, *Chem. Soc. J.*, 1872, 264), whilst, however, Fresenius (*Zeitschr.*, x, 133,



*Chem. Soc. J.*, 1872, 326) found only .54 per cent. of phosphoric acid dissolved from phosphorite by treatment with ammonium citrate, the author obtained 2.43 per cent. as a mean. The action of ammonium succinate was also tried on the phosphates of iron, alumina, and lime, but was found to possess comparatively slight solvent power.

E. K.

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**Examination of Bleaching Powder.** By F. CRACE CALVERT  
(Compt. rend., lxxiv, 1411).

THE author effects the analysis by extracting with water a known weight of the powder, treating the filtrate with carbon dioxide, and boiling to decompose bicarbonate. The precipitated calcium carbonate represents the quantity of hypochlorite, while the calcium chloride remains in solution, and may be determined by silver nitrate or by evaporation to dryness, and fusion. The average results give 1 part hypochlorite to 2 of chloride.

C. G. S.

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**Volumetric Estimation of Zinc.** By A. HENNINGER (Bull. Soc. Chim. de Paris, xvii, 112—114.)

SCHAFFNER's process for estimating zinc consists in precipitating an ammoniacal solution of that metal with a standard solution of sodium sulphide, the point of complete precipitation being ascertained by the tint produced by a slight excess of the precipitant upon paper impregnated with certain salts, generally ferrous oxide, lead carbonate, or salts of nickel or cobalt.

The author, not getting satisfactory results with the kind of paper ordinarily employed, tried that used for *cartes de visite*. This is made by covering the paper with a layer of white lead, and then passing it under hot rollers. With this paper it is easy to detect a quantity of sodium sulphide equal to .002 grm. of zinc in half a litre.

B. J. G.

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**Detection of Nitrobenzene in Bitter Almond Oil.** By EDM. BOURGOIN (Bull. Soc. Chim. de Paris, xvii, 243).

BITTER almond oil is often adulterated with nitrobenzene.\* Although the densities of these two substances are different, yet the specific gravity cannot be relied on as a test of purity, since alcohol may also have been added.

The author thought that aniline would be formed by distilling the oil containing nitrobenzene in presence of nascent hydrogen. But, although the slightest trace of pure nitrobenzene furnishes a distillate giving a deep violet-blue with calcium hypochlorite, the presence of bitter almond oil prevents this reaction to such a degree that a sample containing 40 per cent. of nitrobenzene gives a negative result when treated as above.

The author finds that agitating the suspected oil with half its weight

\* Nitrobenzene is sometimes sold under the name of "artificial oil of almonds."

of caustic potash is a most delicate test of purity. If nitrobenzene is absent, only a yellowish colour is produced; if present, the yellow becomes first yellowish-red, and then green. On adding water, the mixture separates into two layers, the lower yellow, and the upper green.

B. J. G.

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**Estimation of Uric Acid.** By H. SCHWANERT (*Ann. Chem. Pharm.*, clxiii, 153—159).

THE author confirms the statements made by Salkowski (*Zeitschr. Anal. Chem.*, x, 248), that, after treatment with hydrochloric acid, a further quantity of uric acid can be precipitated by adding ammonia and silver nitrate. He finds, however, that the additional quantity of uric acid thus to be obtained can be calculated from the experiments of Voit and Zabelin (*Ann. Chem. Pharm., Suppl.*, ii, 313), who have shown that the quantity of the uric acid not precipitated by hydrochloric acid is proportional to the total volume of the acidified liquid and the wash-waters, and equal to 0.0045 grm. per 100 c.c. of liquid. He therefore recommends the making of a calculation upon this datum, instead of employing Salkowski's silver process, as being quite as accurate, and effecting a saving of much time.

He also points out that recent determinations of uric acid are probably more accurate than Salkowski supposes, inasmuch as since the publication of Voit and Zabelin's investigations seven years ago, allowance has been made for the uric acid not precipitated by hydrochloric acid.

E. D.

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**Estimation of Uric Acid.** By G. SALKOWSKI (*Deut. Chem. Ges. Ber.*, v, 410—411).

A NOTE correcting Schwanert's opinion on the author's previous researches on this subject (see this Journal, x, 333). The amount of uric acid not precipitated by hydrochloric acid is not, as the author before remarked, a constant quantity.

M. M. P. M.

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**Quantitative Estimation of Egg Albumin.** By P. LIBORINS (*Chem. Centr.*, 1872, 153).

THE author reviews the various proposed methods. Those of Scherer and Berzelius give results too low, because certain modifications of the albumin escape estimation. Precipitation by alcohol gives the most trustworthy results. Hœbler's method is inaccurate. Hoppe-Seyler's polarisation method is not generally useful, because different modifications of egg albumin, especially as existing in urine, have different specific rotatory powers. The method of Méhu introduces serious errors. Serum-, egg-, and blood-albumin, also casein from milk, form a determinate compound with tannin, so that by titration with a standard tannin solution tolerably concordant results are obtained; but

in treating urines in this manner, great discrepancies were noticed in the results.

M. M. P. M.

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**Ceroso-ceric Oxide as a Test for Strychnine.** By L. DJÜRBERG (Chem. Centr., 1872, 153).

THE author has repeated Sonnenschein's experiments. He finds that the ultimate colour obtained in using this test is a yellow-red, not cherry-red.

To make the ceroso-ceric oxide, the author dissolves cerium oxalate (the Swedish official oxalate) in hydrochloric acid, warming gently; oxidises with sodium hypochlorite; precipitates with sodium hydrate; and treats the precipitated cerous hydrate again with sodium hypochlorite, whereby ceroso-ceric oxide is formed, which is collected, dried, and powdered.

M. M. P. M.

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**Means of Distinguishing Grape from Fruit Wine** (Chem. Centr., 1872, 153).

WITH ammonia (9 parts wine to 1 part ammonia), after a few hours, fruit wine gives well formed crystals adhering to the sides of the vessel—under the microscope these are seen to be regular tables—grape wine gives a white powdery precipitate, falling to the bottom of the vessel—seen by the microscope to consist of minute star-shaped crystals. Both precipitates are soluble in dilute acetic acid, a solution of the former giving a white precipitate with ammonium oxalate; of the latter, a similar precipitate, but smaller in amount, and in the filtrate therefrom a precipitate is formed by ammonia, which is not the case with the solution of the fruit wine crystals. Phosphate of calcium is present in fruit wine; phosphate of magnesium in grape wine.

M. M. P. M.

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**Technical Chemistry.**

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**Well-Water of Towns.** By C. AEBY (J. pr. Chem. [2], v, 206—214).

THE author has examined the wells and springs of Bern and Magdeburg, with the view of determining their sanitary value as drinking waters. In these waters the quantities of sulphuric acid and chlorine are together always slightly more than sufficient to neutralise the potassium and sodium, so that the quantity of the latter can be estimated by determining that of the former constituents. He considers that the sulphuric acid is present as alkali-sulphate, and not any as gypsum; for, as magnesium carbonate is disseminated through the soil, and as gypsum in solution reacts with magnesium carbonate, it would, if present in the water, cause a certain relation to exist between the dissolved mag-



nesium and the sulphates. The magnesium, he considers, exists in the water as carbonate and a very little sulphate, and the calcium as carbonate and nitrate.

The well-waters of towns therefore contain, in addition to the usual constituents of spring-water, calcium nitrate, potassium sulphate, and sodium chloride, so that an increase in the quantities of these salts indicates an increase in the amount of organic impurities present.

The paper is accompanied by a tabular statement of the composition of the numerous waters analysed.

E. D.

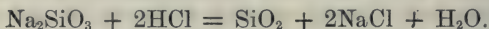
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**Commercial Manufacture of Chlorine.** By F. DE LALANDE and MAURICE PRUD'HOMME (Bull. Soc. Chim. de Paris, xvii, 290).

WHEN silica is heated with an alkaline or earthy chloride to a red heat in a current of oxygen or dry air, chlorine is evolved, and a silicate of the base of the chloride is formed—



By passing over the mixture hydrochloric acid together with the oxygen, the chloride is reproduced by the decomposition of the silicate, and thus a continuous evolution of chlorine is caused.

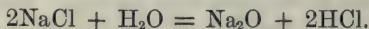


The water-vapour formed in this reaction gives rise to two secondary reactions.

1. The water is decomposed by the chlorine,



2. The chloride is decomposed by the water,



Boric, stannic, and phosphoric acids, alumina, pumice-stone, fragments of brick, &c., cause the evolution of chlorine quite as well as silica.

The temperature of the reaction is higher than in Deacon's process, but the quantity of chlorine evolved is the same.

J. B.

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**The Salt-gardens and Salt Trade of Portugal.** By AIMÉ GIRARD (Compt. rend. lxxiv, 1195—1199).

PORTUGAL is essentially a salt-producing country, favoured by its warm climate, and by the dry north-east winds which prevail upon its coast-land; it produces annually, by the evaporation of sea-water alone, more than 250,000 tons of salt. The manufacture, of which the following is a brief outline, is conducted principally in the districts surrounding Sétubal, Lisbon, Aveiro, and Les Algarves.

A considerable tract of land, from 1 to 2 hectares in extent, is divided off into a number of shallow ponds, each presenting an evaporating surface of about 100 square meters, and a depth of 20 centi-

meters; the whole series communicating with a large reservoir, from which a constant supply of sea-water can be obtained. Towards the close of the year, when the salting season is over, the salt-gardens are flooded with water to a depth of 50 or 60 centimeters. Evaporation proceeds slowly during the winter, and during the ensuing spring, so that about the month of June, the separate reservoirs begin to appear above water. These are then carefully cleansed, and the evaporation allowed to go on until the salt becomes nearly dry. The saline mass, which is about 3 or 4 centimetres in thickness, is then removed, and sent into the market without any further purification. This is the first crop.

A fresh supply of water having been allowed to flow in from the large reservoir, in twenty days a second crop is collected, varying from 2 to 3 centimeters in thickness; the evaporation is not, however, as in the preceding case, conducted almost to dryness, but the salt is gathered under a layer of at least 2 centimeters of water. In like manner a third crop is, if possible, obtained, and finally, towards the end of September, the land is flooded in the manner previously described.

It might be supposed that, inasmuch as the mother-liquors are never removed from the land, the gradual accumulation of magnesian salts would eventually render either the extraction of salt impracticable, or the product worthless. Such, however, is not the case; the magnesian salts do not increase, but, on the contrary, gradually disappear, their disappearance being due to a somewhat curious phenomenon.

Upon the bottom of the salt-gardens there has grown from time immemorial, a compact felting or sod, from 2 to 3 mm. in thickness, due to the vegetation of a peculiar marine thallogen; the development of this sod is found to be indispensable to the purification of the water.

The uniformly continuous surface which it presents appears to act as natural dialytic diaphragm, through which magnesium chloride penetrates more rapidly than sodium chloride. A gradual but constant separation of these salts, therefore, ensues, which is necessarily more complete the longer the water is allowed to remain in contact with the soil. It will now be apparent that although, in the preparation of the first crop of salt, the evaporation is carried nearly to dryness, the yield is likely to be more free from magnesian salts than the second and third crops, in which the water is evaporated more rapidly, and the time for dialytic action consequently curtailed.

The author has verified the above hypothesis by direct experiment. Mixed solutions of sodium and magnesium chlorides were submitted to dialysis, upon the ordinary medium, in such a manner as to resemble as far as possible the natural process of the salt-gardens. The ratio of magnesium to sodium chloride was found to increase steadily in the diffusate, thus placing beyond doubt the fact that the spontaneous purification of the water during the winter months is due to an action which closely resembles, if it is not identical with, dialysis.

Analyses of the salts of Sétubal, where the foregoing method of extraction is especially adopted, show the first crop to contain 98 per cent., and second and succeeding crops, about 94 per cent. of sodium chloride, the magnesium chloride increasing from 0.2 to

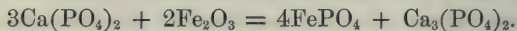
1.9 per cent. respectively. The salts of Lisbon and Aveiro are very nearly, if not quite, equal to those of Sétubal.

J. W.

**The Part which Ferric and Aluminic Oxides play in the Manufacture of Superphosphates; and the Comparative value of Mineral Phosphates.** By T. L. PATTERSON (Chem. News, xxv, 255—257, and 268—270).

UP to the present time, manufacturers of artificial phosphatic manures have, as a rule, estimated the value of the raw material solely with reference to the percentage of tricalcic phosphate. They have paid little or no attention to the remaining constituents of the mineral, but, relying upon the knowledge afforded by a partial analysis, have anticipated not only to be able to convert the whole of the insoluble phosphate directly into the soluble variety, but to ensure indefinitely the stability and value of the converted product. In the present communication, the author points out certain fallacies connected with the above suppositions, showing more especially that the presence of ferric and aluminic oxides in the mineral not only renders a considerable portion of the phosphoric acid unavailable, but exerts also a deleterious influence upon the manufactured product.

In a series of experiments, the details of which are unimportant, the author adduces evidence, proving that the iron does not pre-exist in the mineral as ferric phosphate, but that it is present as oxide, partly in the hydrated and partly in the anhydrous condition. That during the process of manufacture, and according to well-known reactions, a considerable proportion of the iron is converted into ferric phosphate, at the expense of the tricalcic salt, and that inasmuch as ferric phosphate is perfectly insoluble, the proportion of phosphoric acid so combined, must be considered as a direct loss both to the manufacturer and to the agriculturist. Further, that when a neutral solution of ferric or aluminic sulphate is digested with tricalcic phosphate, or a neutral solution of the phosphate digested with ferric oxide, in either case combination between the iron and phosphoric acid is slowly brought about and a proportion of the phosphoric acid rendered insoluble. Upon this latter reaction, he bases an opinion respecting the "reduction" which takes place when superphosphates are preserved for a length of time. The ferric oxide which was unattacked during the process of converting the insoluble phosphate into the soluble variety, is supposed to react slowly upon the monocalcic phosphate, to absorb in this way a proportion of the phosphoric acid, and at the same time to reproduce a corresponding quantity of insoluble tricalcic phosphate—



As this reaction is sufficient to account for all the phenomena observed, it is on the whole—notwithstanding the improbability of the formation of calcium metaphosphate—considered more probable than the suggestion of Fresenius, who supposed dicalcic phosphate to be produced, thus—





Respecting the estimation of reduced phosphates by the use of ammonium citrate, the details of several experiments are quoted, showing that the proportion of phosphate which had really reverted to the insoluble condition was in some instances less by one-half than the quantity actually obtained by analysis, the reason being that the solution of ammonium citrate dissolves not only the recently precipitated, but also the original ferric phosphate, and thus reckons as reduced phosphate a salt which had been from the first perfectly insoluble.

The latter portion of the paper is devoted to the calculation of the comparative value of mineral phosphates. Direct experiment having demonstrated the absolute insolubility of ferric and aluminic phosphates, even under natural conditions the most favourable for their solution, it is assumed that they are useless as fertilising agents: and knowing, moreover, that every per cent. of iron in the mineral represents a corresponding loss of calcium phosphate, it is found necessary, in order to calculate the net realisable percentage of calcium phosphate in a sample, to ascertain first by analysis the actual percentage of calcium phosphate, ferrous, ferric, and aluminic oxides, and to calculate for each of the oxides an equivalent quantity of calcium phosphate. Then, deducting the sum of the three, from the actual percentage of that earth, the remainder will represent in terms of calcium phosphate, the comparative value of the sample in question.

To obtain the correct money value of the phosphate, another deduction must, however, be made, viz., the value of the vitriol required for the preliminary conversion of the above oxides, as well as of the calcium carbonate into sulphate. This calculation, as well as the preceding one, is too simple to need detailed description; however, a number of examples will be found in the original paper, showing the manner in which these corrections may be most readily performed.

It will be seen then that the actual value of a mineral phosphate depends, not as has been hitherto supposed, solely upon the percentage of tricalcic phosphate, but also to no inconsiderable extent upon the presence or absence of certain other constituents. Indeed, in some samples examined by the author, a difference of 75 per cent. was observed between the actual and apparent values, when the former was estimated according to the system above described, and the latter by the method in general use. J. W.

**New Method of preparing very High Grade Superphosphate from the Mejillones-Guano (so called "Concentrated Superphosphate").** By HERM. VOHL (Dingl. Polyt. J., cciii, 491—493).

ALMOST all superphosphates are prepared by the decomposition of the tribasic calcium phosphate by sulphuric acid, and in this way it is impossible to avoid weakening the product by the presence of calcium sulphate,  $\text{CaSO}_4 + 2\text{H}_2\text{O}$ . Many manufacturers find it very desirable to have at hand extremely high grade, i.e., concentrated superphosphates, and these can only be obtained by preventing the formation of the hydrated calcium sulphate. To this end, a quantity of Mejillones-guano was treated with dilute phosphoric acid, so that 1 or 2 molecules

of lime were saturated as desired, a mixture of neutral and acid phosphates being obtained. If a very concentrated superphosphate is made, it must be packed in casks, as it is very hygroscopic. W. S.

### Enamel for Copper Cooking Vessels. (Dingl. Polyt. J., cciii, 499—500).

To enamel the insides of copper vessels in which acid fruit and vegetables are cooked, and so prevent the formation of the so-called "verdigris," the following method is recommended:—12 parts of white fluorspar, 12 parts unburnt gypsum, and 1 part borax are finely powdered, intimately mixed and fused in a crucible. The fused mass is then poured out, and after cooling is rubbed up to a paste. The copper vessel is then coated inside with this preparation, which is applied by means of a brush, and the vessel is placed in a moderately warm place, so that the coating may dry uniformly, when it is subjected to a gradually increasing heat, till at length the preparation fuses. On cooling, the vessel is found to be protected internally by a white, opaque enamel, adhering very firmly to the copper, not chipping off by ordinary knocking and rubbing, and impervious to vegetable acids. W. S.

### Formation of Corrosive Sublimate in Mixtures containing Calomel. By G. VULPIUS (Chem. Centr., 1872, 147).

In mixtures of calomel with milk or cane-sugar, magnesia, hydrated carbonate of magnesium, or sodium bicarbonate, no formation of corrosive sublimate takes place in 24 hours. In three months no corrosive sublimate is formed in any of the above mixtures, except in the case of calomel with sodium bicarbonate and milk-sugar, when there are traces of corrosive sublimate, and of sodium bicarbonate with cane-sugar, when the quantity of sublimate is considerable. By digesting with water mixtures containing calomel and magnesia or sodium bicarbonate, corrosive sublimate is formed—if the waters contain a little hydrochloric acid, this formation is much checked—calomel alone digested for a short time with water containing a little hydrochloric acid does not give corrosive sublimate.

Pepsin does not cause the formation of the sublimate, but if it be in solution in small quantity, causes it to become insoluble.

M. M. P. M.

### Use of Quick Lime in the Blast Furnace Mixture.

By J. GRUNER (Dingl. Polyt. J., cciv, 39—47).

THE object of this paper is to show that in order to effect the greatest economy in fuel in the blast furnace operations, instead of using raw limestone, raw iron ore, &c.:—

1stly. The limestone should be well calcined (*i.e.*, converted into quicklime), and it is recommended that this be done separately in a Hofmann's circular furnace, in which the calcining may be performed most economically as regards fuel.

2ndly. The raw iron ores should be also well dried, and freed from carbonic acid by roasting separately.



3rdly. The fuel should be perfectly dry.

By carefully observing the above directions, at least 50 kilograms of coke per ton of pig-iron may be saved.

On the average a third, and occasionally a half, of the total carbon dioxide evolved in the blast furnace (liberated in the reduction of the ore, and in the decomposition of the limestone) is reduced by contact with the glowing coke, to carbon monoxide. This reduction of the carbon dioxide takes place especially in the lower zones of the furnace, where the reduction of the ferric oxide is completed, whilst the decomposition of the calcium carbonate occurs in the upper or middle zones. It is therefore perhaps more probable that the carbon dioxide which undergoes *partial deoxidation*, is that liberated in the reduction of the ore, than that from the decomposition of the limestone. Nevertheless, the author considers that at the least a quarter of the total carbon dioxide contained in the limestone is reduced to carbon monoxide, but he by no means coincides with Mr. I. L. Bell, who states that the *whole* of it escapes as carbon monoxide.

The next inquiry relates to the effect of the presence of water in the materials for the blast furnace mixture.

If calcium hydrate has been formed in the upper part of the furnace, its decomposition may occur in two ways, viz., the water may be liberated as steam, or it may be at once decomposed into hydrogen and oxygen in contact with the red-hot carbon. As the decomposition of the calcium hydrate requires a higher temperature than that of the calcium carbonate, it follows that the aqueous vapour will be as thoroughly reduced as the carbon dioxide. The loss of heat is partially compensated for in this case by the fact that the liberated oxygen of the water gives out a portion of heat in combining with the carbon to form carbon monoxide.

If it be assumed that the amount of limestone per ton of pig-iron required is 600 kilos., then if the limestone has been burnt separately, there will be an expenditure of 29.76 *kilos. of pure carbon*, whereas if the unburnt limestone is used, 97.62 *kilos.* will be required.

From 100 kilos. calcium carbonate 44 kilos. carbon dioxide may be liberated, and these, for their reduction to monoxide, will require

$\frac{\frac{3}{11} \times 44}{4} = 3 \text{ kilos. pure carbon,}$  if it be assumed that only  $\frac{1}{4}$ th of the carbon dioxide suffers this reduction.

Then, per ton of pig-iron or 600 kilos. limestone, there will be further required  $6 \times 3 = 18$  kilos. pure carbon.

But besides the carbon required, an absorption of heat takes place, a loss which must be restored to the blast furnace :—

1 kil. C combined with $\frac{8}{3}$ kil. O.	
Yields $\frac{11}{3}$ kil. CO <sub>2</sub> , and liberates .....	8080 heat-units
2 kil. C combined with $\frac{8}{3}$ kil. O, yield	
$\frac{14}{3}$ kil. CO, and liberate thus only	
$2 \times 2473 =$ .....	4946 „

*Loss of heat expressed by this deficiency* = 3134 „

Thus it follows that the heat absorbed by the reduction of every kilo. of CO<sub>2</sub> to CO will be  $\frac{3}{11} \times 3134 = 855$  heat-units, or for every



kilo.  $\text{CaCO}_3$   $\frac{0.44 \times 855}{4} = 94$  heat-units, assuming that only  $\frac{1}{4}$ th of the  $\text{CO}_2$  is reduced to  $\text{CO}$ . This will be, per ton of pig-iron,  $600 \times 94 = 56400$  heat-units, the equivalent of which in carbon (burnt to  $\text{CO}$ ) will be  $\frac{56400}{2473} = 22$  kilos. These 22 kilos. added to the 18 already accounted for = 40 kilos. of carbon per ton of pig-iron, using 600 kilos. limestone; and further, if raw limestone be used ( $97.62$  kilos. +  $40$  kilos.) =  $29.76$  kilos. =  $107.86$  kilos. carbon, deducting that used in calcining the limestone. This number is actually the minimum, as on the average more than  $\frac{1}{4}$ th the total carbon dioxide of the limestone is reduced to monoxide. According to the preceding, the employment of burnt lime guarantees a diminution of close upon 10 per cent. in the weight of fuel required. This reduction, though it cannot fully be realised in actual practice, may still be approached very nearly by studiously following the directions here given.

According to Favre and Silbermann, 1 kilo. of lime converted into hydrate, liberates  $143.9$  heat-units; this gives  $109$  heat units as that absorbed in the decomposition of 1 kilo. of calcium hydrate. The hydrate in its decomposition absorbs  $37 \times 109 = 4033$  heat-units. Further, assuming that the water is entirely reduced, then, in its decomposition the same amount of heat is necessary which is expressed by the combustion of an equivalent of hydrogen, minus that which is furnished in the combination of the oxygen of the water with carbon to form carbon monoxide.

1 eq. hydrogen yields .....	34467 heat-units.
1 eq. carbon $6 \times 2473$ .....	<u><math>= 14838</math></u> „

Leaving for the decomposition of the water into H and O .....	<u><math>19629</math></u> „
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Consequently, for the decomposition of calcium hydrate into calcium oxide, hydrogen, and carbon monoxide,  $19629 + 4033 = 23662$  heat-units.

The bare decomposition of 1 mol. calcium carbonate requires $50 \times 373.5$ .....	$= 18675$ heat-units
For the complete reduction of the $\text{CO}_2$ to $2\text{CO}$ , per eq. of C, $6 \times 3134$ .....	<u><math>= 18804</math></u> „

For the complete decomposition of the $\text{CaCO}_3$ into $\text{CaO}$ and $2\text{CO}$ .....	<u><math>37479</math></u> „
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It follows therefore that the decomposition of the hydrate requires a smaller amount of heat, than that of the carbonate, assuming an equal absorption of solid carbon on both sides; but as the carbon appears to act more powerfully on the water than on the carbon dioxide, in consequence of the higher temperature at which the hydrate gives up its water, it is very probable that as much carbon is necessary for the decomposition of the hydrate as for the carbonate, and hence the importance of guarding against the presence of aqueous vapour also, in the gaseous current permeating the materials in the blast furnace.

W. S.

**Preparation and Purgative Properties of Sodium Sulphovinate.** By LIMOUSIN (J. Pharm. [4], xv, 271; Pharm. J. Trans. [3], ii, 985).

THE medicinal advantages of this salt were pointed out by Dr. Rabuteau in 1870. Its cost by the ordinary process was 45 francs per kilogram, but the author has since discovered a more economical method.

Introduce slowly and simultaneously into a flask kept cool, equal weights (1 kilogram) of sulphuric acid and pure strong alcohol, the latter being maintained in excess, heat for five days to  $23^{\circ}$ , dilute with 5 litres of water, saturate with barium (not calcium) carbonate, decant and filter. Precipitate the filtrate with sodium carbonate, decant, filter, evaporate at  $100^{\circ}$  to sp. gr. 1.33, and allow to crystallise. The crystals (about 1 kilogram) are hexagonal tables, of the formula  $C_2H_5NaSO_4 + H_2O$ , permanent in air when pure, soluble in their own weight of water at  $18^{\circ}$ , freely soluble in dilute spirit and glycerin, sparingly in absolute alcohol, not at all in ether, decomposed at  $180^{\circ}$  into alcohol and sodium disulphate. In dissolving they decrease the temperature  $13^{\circ}$ . The solution is stable below  $120^{\circ}$ , has a cool sweetish taste, and is three times more powerful as a laxative than sodium sulphate.

C. G. S.

**Decolorising Action of Nitric Acid on Red Wines.** By FAUSTO SESTINI (Versuchs-Stationen Organ, xv, 9—13).

GENUINE red wines of Friuli and the Romagna are quickly decolorised by the process of Fantaggini and Cottini, viz., heating 50 c.c. of the wine with 6 c.c. nitric acid, sp. gr. 1.38, to  $90^{\circ}$ — $95^{\circ}$  C.

The decoloration is considerably delayed by performing the operation in closed vessels, as also by the addition of alcohol, tartaric acid or tannic acid. This process for distinguishing between genuine and artificially coloured wines is therefore not trustworthy.

E. K.

**Aniline Black.** By H. RHEINECK (Dingl. Polyt. J., cciii, 485—489).

ANILINE black is obtained by the oxidation of aniline and aniline-oils, and is analogous in its mode of formation to the other aniline colouring matters. This oxidation is always attended with a molecular condensation, resulting from the combination of several molecules of aniline and toluidine, &c. The same thing occurs undoubtedly in the formation of aniline black. Further, these oxidation-products of aniline and its homologues, the aniline colouring matters, are always of basic nature. The author has found that aniline black is a well defined base, and suggests that it might be called *Nigraniline*, as the base of aniline red is named rosaniline. A. Müller prepares aniline black by warming a mixture of 20 grms. potassium chlorate, 40 grms. cupric sulphate, 16 grms. ammonium chloride, 40 grms. aniline chloride, and 500 c.c. of water, to  $60^{\circ}$ , whereupon the formation of a black quickly follows. The author found that an equally beautiful black could be obtained without



the use of ammonium chloride. He brought together at the ordinary temperature aniline hydrochloride, potassium chlorate, a minute quantity of cupric chloride, and a sufficient quantity of water. This mixture was allowed to evaporate spontaneously, and at the ordinary temperature, till, as a sign of the completion of the process, a dry, black powder was obtained. Aniline, hydrochloric acid, and potassium chlorate were employed in equal weights, and in the black mass obtained, unaltered crystals of potassium chlorate were found. In the acid aqueous solution, aniline could no longer be detected, but ammonia was found. After washing with hot water, the black powder burnt without residue. The aniline employed contained toluidine, and furnished 120.5 per cent. of the washed black powder.

The colour, as at first communicated to the fabric, appears of a dark green, but after treatment with alkalies, this colour changes to dark violet. The dark green body is the hydrochloride of the aniline black, and the dark violet body the free base itself. With soda or ammonia, 8.9 per cent. of hydrochloric acid can be extracted, therefore the molecular weight of the hydrochloride is about  $100 \times \frac{36.5}{8.9} = 410$ , and

that of the free base 373.5. This base has the power of abstracting the acids from the salts of aniline. A small piece of cotton, on which a very thin layer of the dark violet colour is brought, is immediately coloured green by aniline hydrochloride, even in presence of excess of aniline. A piece of cotton, moderately coloured with aniline black is a good test for the presence of free acids or alkalies, and the same piece may be used several times without losing its colour. When turned green by an acid, it should be well washed with distilled water, when it will be found to change quickly to violet, in presence of an alkaline solution as weak as that found in spring water. The black green body (not treated with alkalies) treated with concentrated sulphuric acid, gives off hydrochloric acid gas, and yields a violet solution, which on evaporation leaves a black-green residue, doubtless the sulphate.

With pure aniline only 114.8 per cent. of aniline-black was obtained (against 120.5), and it may be assumed that toluidine enters into the composition of the aniline-black molecule. The black obtained was of a very poor character, as well as small in quantity. W. S.

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**Aniline Black.** By JOHN LIGHTFOOT (Dingl. Polyt. J., cliii, 483—485).

THAT the presence of copper in some form is absolutely necessary for the formation of aniline black, has been hitherto universally acknowledged. All black colours believed to be formed without the aid of copper really owe their formation to its presence in the vessels in which they are prepared, or in the rollers employed in printing.

Mere traces of copper are sufficient to produce a black colour, but the presence of this metal in some quantity is indispensable. Cupric sulphate was first used, but for various reasons was subsequently replaced by cupric sulphide.

In order to discover the effect of employing different metals in the formation of aniline black, a number of experiments were tried, a



basic aniline salt being used. To ascertain if an aniline salt is acid, Dale's magenta paper is recommended, made by soaking ordinary filter paper in a weak fuchsine solution. A trace of acid turns the red colour yellow. The experimental mixture consisted of *aniline hydrochloride* and *ammonium chlorate*, thickened with starch. This mixture was printed by a wooden roller on well bleached cotton, and whilst the fabric was still damp, the following metals were brought in contact with it, and allowed to remain so for 15 minutes:—Copper, iron, vanadium, uranium, nickel, lead, zinc, antimony, tin, manganese, chromium, bismuth, arsenic, titanium, tungsten, cadmium, tellurium, molybdenum, mercury, silver, gold, platinum, palladium, rhodium, iridium, aluminium, osmium, cobalt, ruthenium, thallium, magnesium, lithium, lanthanum, didymium, erbium, yttrium, selenium, tantalum, niobium. After this, the fabric was hung up in a warm and damp place for 12 hours, and then passed through an alkaline bath. The result was that the best black was obtained with vanadium, next with copper, then with uranium, and lastly with iron. All other metals give either very little colour or none at all. A sovereign and a shilling previously found to have no effect, were shaken in a bag with some copper coins, and then placed in contact with the piece of cotton, when the sovereign produced a grey, and the shilling an almost black tint.

W. S.

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**Indulin Blue.** By C. PFUNDHELLER (Dingl. Polyt. J., cciii, 506).

INDULIN (*Dingl. Polyt. J.* (1870), xcvi, 190) is dissolved with careful trituration in water, and is then boiled with 50 to 100 parts of water. A bath is made feebly alkaline with borax or soda, the solution of the colouring matter is added, and the wool is treated therein at a temperature below the boiling point of the solution, till a sample taken out and washed in water acidified with sulphuric acid, shows the required shade. The whole portion of wool is then taken from the bath, drained, washed, and dipped in a boiling solution of sulphuric acid and chloride of tin, when the blue colour is quickly developed. After short boiling the operation is finished.

W. S.

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**New Mode of Printing upon Stuffs by Means of Metallic Precipitations.** By E. VIAL (*Compt. rend.*, lxxiv, 486).

If any tissue of cotton, silk, &c., be dipped in a solution of silver nitrate, slightly dried, and placed under a stereotyped plate of zinc, lead, or copper, the nitrate will be decomposed at the parts where contact ensues, and a faithful and indelible image will be imprinted upon the stuff. A silvered copper plate, engraved, will impart its pattern to stuff so prepared with the greatest precision. The tint of the printing can be varied at will from a light grey to a deep black, according to the strength of the solution of silver nitrate, and to the metal used for precipitation.

J. B.

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**New Photo-lithographic Method** (*Dingl. Polyt. J.*, 503—504).

THE operation described is based on the property of gelatin, even in

thin layers, to resist printing ink, and on the fact that this ink is easily removed from the lithographic stone. A piece of ordinary gelatin paper, such as is used in carbon printing, is made sensitive in the ordinary manner in a bath of potassium dichromate, and exposed to light under the positive intended for lithographing. After exposure, the paper is immersed in water for some seconds, laid with the gelatin side on a well polished lithographic stone, and the excess of water wiped off. Some minutes later water at 36° is poured over it, and the picture is thereby developed as usual, the paper being gradually removed by the warm water. Warm water is then cautiously poured over the stone, and the soluble gelatin is thus removed. The picture being well developed, alum water is poured over the stone, and the latter is allowed to dry, when the negative obtained should be quite sharply and clearly defined. The edges of the stone are now protected with gum, and lithographic printing ink is applied. The gelatin is next removed by wiping the stone with a flannel soaked in gum-water. A positive of great beauty may finally be obtained, if all conditions have been fulfilled.

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W. S.

**Pyrophotography.** By Dr. OIDTMANN (Dingl. Polyt. J., cciii, 489—491).

THE photographic preparation and reproduction of pictures on fusible surfaces, with fusible colours, is the principle of this art; and the author has applied it on the large scale to monumental mosaic glass staining, and for that required for the windows of churches.

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W. S.

**New Method of Reproducing Drawings.** By B. RENAULT (Compt. rend., lxxiv, 1412).

THE design being traced with adhesive ink on strong glazed paper, bronze powder is dusted over, and adheres to the marks. The drawing is now applied to the surface of a sensitized paper, which is blackened by the reducing action of the metallic powder. By exposure to the vapour of alcohol, the ink of the original can be again rendered adhesive, and the operation can be thus repeated many times.

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C. G. S.

**To Render Cloth and other Material Waterproof, and Protect them from Moths.** (Dingl. Polyt. J., cciii, 506—507).

TEN POUNDS of alum and 10 of lead acetate are dissolved in sufficient warm water, and the mixture allowed to stand, till the precipitate of lead sulphate has settled down. The clear solution containing aluminium acetate is poured off, and mixed with 500 measures of water, in which dissolved isinglass is stirred up. The articles to be made waterproof are steeped in this mixture for 12 hours, after which they are dried, and subjected to pressure. Clothing made of such material does not interfere with the perspiration of the body.

W. S.

## PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XXX.—COMMUNICATIONS FROM THE LABORATORY OF  
THE LONDON INSTITUTION.No. V.—*On the Nitration-products of the Dibromophenolsulphonic Acids.*  
(First Notice.)

By HENRY E. ARMSTRONG and FRED. D. BROWN.

THE nitration-products of the dichlorophenolsulphonic acid obtained by chlorination of Kekulé's phenolparasulphonic acid have already been described by one of us (this *Journal*, ix, 1112); in the present communication the results of the examination of the corresponding brominated compound are stated.

The products we have obtained are, as was anticipated, the precise analogues of those yielded by the chlorinated acid, but several not uninteresting observations have been made, showing that, although identical in kind, the reactions in the two instances are in several respects different in degree.

It had previously been found (*ibid.* x, 13) that the chlorodinitrophenol prepared from ordinary  $\alpha$ -dinitrophenol was identical with the main product of the action of nitric acid on dichlorophenolparasulphonic acid, the corresponding bromo-derivative of  $\alpha$ -dinitrophenol has therefore been examined and compared with the bromodinitrophenol obtained by nitration of the dibromosulpho-acid, with the result that they also are identical.

The phenolsulphonic acid employed was prepared by heating a mixture of equal weights of phenol and ordinary concentrated sulphuric acid for 15 hours at 100°, the heating being continued thus long in order to ensure the conversion of the phenolmeta- into the phenolpara-sulphonic acid, with what success will afterwards be apparent. The product was dissolved in water, and, after the small quantity of sulphuric acid present had been removed by lead carbonate, &c., the free acid was neutralised by potassium carbonate, and the solution evaporated to the crystallising point. The first crystallisation of the potassium salt thus prepared was separated from the mother-liquor by draining on a vacuum-filter, and afterwards twice recrystallised. Only this purified salt was made use of in the following experiments.

Even when bromine is made to act on an aqueous solution of potas-



sium phenolparasulphonate in the proportion necessary to form the monobrominated derivative, the main product consists, as shown by Senhofer (*Ann. Chem. Pharm.*, clvi, 102), of potassium dibromophenolsulphonate, a very small proportion only of the monobrominated salt being produced; we find that by employing the proportions— $2\text{Br}_2 : \text{C}_6\text{H}_4(\text{OH})\text{SO}_3\text{K}$ —an almost theoretical yield of dibromophenolsulphonate is obtained.

*Preparation.*—The potassium phenolsulphonate is dissolved in water, and the bromine is added by small quantities to the *cold* solution, the liquid being constantly agitated. The flask containing the solution should be immersed in cold water, in order to prevent the accumulation of the heat evolved in the reaction. The bromine disappears rapidly on agitation, the solution becoming colourless, and it is not until almost the whole of the necessary quantity has been added that it assumes a permanent yellow colour. The dibromo-salt separates out partially, either during the addition of the bromine, or some time afterwards, according to the state of concentration of the solution employed. It is usually in so finely divided a state, however, that it is a matter of extreme difficulty to separate it from the mother-liquor, so that it is advisable to heat and to add water until the whole is dissolved; on cooling, the potassium salt then crystallises out in needles, and a further large quantity is obtained on evaporating the filtrate.

If care be taken to avoid all rise of temperature on the addition of the bromine, the product which separates is entirely soluble in water, but if the bromine act on a warm solution, a certain quantity of an insoluble substance is produced. This melts to an oil under water below  $100^\circ$ ; it is readily soluble in aqueous alcohol, from which it crystallises in long fine needles melting at about  $93^\circ$ . Analysis shows it to be *tribromophenol*, the melting-point of which is stated to be  $95^\circ$ .

·393 grm. of the substance once recrystallised from alcohol gave ·661 grm. AgBr.

·3204 grm. of substance from a second preparation twice recrystallised gave ·542 grm. AgBr.

	Theory.	I.	II.
$\text{Br}_3$ ....	72·50	71·57	71·98

Senhofer also noticed the formation of a small quantity of a substance melting below  $100^\circ$  by the action of bromine on potassium phenolmetasulphonate, but states that it was not obtained of constant composition in different experiments. He regards it as a mixture of higher brominated benzenes, formed by a secondary reaction—this we are much inclined to doubt; evidently the tribromophenol is simply the product of the further action of bromine on the dibromophenolsul-

phonic acid first formed. We also believe that in our case it was formed from a small quantity of meta-salt present in the para-salt we employed, since we noticed that a relatively greater amount was obtained when a salt was acted upon which was known to contain some quantity of potassium phenolmetasulphonate. The dibromophenolpara-sulphonate does not appear to yield tribromophenol when acted upon by bromine at ordinary temperatures.

*Barium Dibromophenolparasulphonate* ( $C_6H_2Br_2OHSO_3$ )<sub>2</sub>Ba + 2 aq.—This salt is readily obtained as a crystalline precipitate on the addition of barium chloride to the solution of the above mentioned potassium salt. Recrystallised from water it forms long, brilliant white, silky needles, which contain two molecules of water, as stated by Senhofer.

·7797 grm. of the air-dried salt lost ·07 grm. H<sub>2</sub>O at 140°.

	Theory.	I.
2H <sub>2</sub> O.....	8·26	8·9

*Sodium Dibromophenolparasulphonate*,  $C_6H_2Br_2OHSO_3Na$  + 2 aq.—We obtained this salt by the direct action of bromine on a moderately dilute cold solution of sodium phenolparasulphonate. It begins to separate out towards the close of the reaction in long, brilliant white needles, easily soluble in hot, difficultly soluble in cold water.

1·8514 grm. of the air dried salt lost ·180 grm. H<sub>2</sub>O at 150°.

1·2338 grm. lost ·1217 grm. H<sub>2</sub>O at 170°.

·383 grm. of the anhydrous salt gave ·4059 grm. AgBr.\*

·4488           "                       "           ·3075 grm. BaSO<sub>4</sub>.

·3758           "                       "           ·0752 grm. Na<sub>2</sub>SO<sub>4</sub>.

	Theory.	I.	II.
2H <sub>2</sub> O ....	9·23	9·72	9·86
Br <sub>2</sub> .....	45·19	44·7	—
S .....	9·03	9·42	—
Na .....	6·49	6·48	—

*Action of Nitric Acid.*—One of the objects of the investigation being to ascertain whether the action of bromine on phenolparasulphonic acid gave rise to the formation of more than one dibrominated-derivative, the salt (either potassium or sodium) acted upon by nitric acid in all the following experiments was a portion of the total product obtained by evaporating the solution to dryness, after the addition of the necessary quantity of bromine.

*Action at 0°.*—The dry salt was added in small portions at a time to nitric acid (sp. gr. 1·36) contained in a flask surrounded by ice, the proportion of acid to salt being about two to one. Under these con-

\* A slight loss of bromine was, by accident, incurred in this experiment.

ditions mere traces only of bromine were evolved. After standing for some hours water was added, and the nitro-product removed by filtration. On heating the filtrate, and afterwards leaving it to cool, no separation of nitro-product was observed, thus proving the decomposition of the sulpho-salt to have been complete. The solid nitro-product was suspended in water, treated with potassium carbonate, and the mixture of potassium salts separated by fractional crystallisation. It was thus found to consist in the main of (a) *dibromonitrophenol* melting at  $132^{\circ}$  (uncorrected), together with small quantities of an isomeric body (c) melting at  $117.5^{\circ}$ , of *bromodinitrophenol* (b) melting at  $117^{\circ}$ , and of the potassium salt of a *bromonitrophenolsulphonic acid* (d).

*Action at higher Temperatures.*—If the salt is added gradually to nitric acid at the ordinary atmospheric temperatures, and the precaution is taken to avoid too great an accumulation of heat by occasionally plunging the flask into cold water, a considerable amount of bromine is set free, but the product still contains a very large quantity of the above dibromonitrophenol (melting point  $132^{\circ}$ ); proportionately more of the dinitrobromophenol is obtained; the same relative proportion of of the isomeric dibromonitrophenol (melting point  $117.5^{\circ}$ ), and little or no bromonitrophenolsulphonic acid.

By the action of a more concentrated acid (sp. gr. 1.42) under the same conditions, a much greater proportion of bromodinitrophenol is produced, but it is not possible in this way to convert the whole of the dibromonitrophenol (melting point  $132^{\circ}$ ) into bromodinitrophenol, without at the same time risking the conversion of more or less of the latter substance into trinitrophenol.

Our observations lead us to conclude that certainly less heat is evolved by the action of nitric acid on potassium dibromophenolpara-sulphonate than on the corresponding dichlorinated compound. On the other hand, the bromo-salt is entirely decomposed by nitric acid at  $0^{\circ}$ , whereas a certain proportion of the chlorinated sulpho-salt always escaped decomposition; at that temperature a comparatively small quantity of the dibromonitrophenol undergoes conversion into bromodinitrophenol by the further action of the nitric acid; a much larger proportion of the corresponding dichloronitrophenol was converted into chlorodinitrophenol, which may doubtless be attributed to the greater amount of heat evolved in the reaction. By the further action of nitric acid, bromodinitrophenol may be converted with moderate ease into trinitrophenol; the corresponding chlorodinitrophenol yields little or no trinitrophenol; it is not attacked by moderately concentrated nitric acid in the cold, and is entirely decomposed by the strongest acid on warming.

Analogous products therefore are obtained by the action of nitric acid upon the dichloro- and dibromo-phenolsulphonic acids prepared from the product of the action of sulphuric acid on phenol; the two



differ only in that they are decomposed with unequal degrees of readiness.

(a.) *Dibromonitrophenol*,  $C_6H_2Br_2NO_2OH$  (melting point  $132^\circ$ ).—There is no doubt that our product is identical with the dibromorthonitrophenol obtained by Brunck (*Zeitschr. f. Chem.* [2], iii, 204) by the action of bromine on orthonitrophenol. He states, however, that it melts at  $141^\circ$ , and is decomposed a few degrees higher; we find the melting point as above, but that decomposition occurs, with evolution of nitric oxide,\* *immediately on fusion*; water is also given off and a brown, friable mass remains, from which at a higher temperature small white shining crystals sublime.

Brunck describes two potassium derivatives of this phenol, one of which is anhydrous, and crystallises in tufts of orange yellow needles; the second, containing 2 molecules of water forms pale-yellow plates. We also have obtained two salts, the one anhydrous and deep orange-yellow, the second containing 2 molecules of water, but crystallised in long yellow prismatic needles, or on slow evaporation of a dilute solution in large prismatic crystals.

We have observed the formation of Brunck's second salt from *impure* solutions, but it has always yielded needles on recrystallisation. The second salt gave the following numbers on analysis:—

1·8556 grm. lost 1848 grm.  $H_2O$   
 ·6137 grm. thus dried gave 1599 grm.  $K_2SO_4$ .

	Theory.	I.
$2H_2O$ ....	9·7	9·9
K.....	11·66	11·69

The phenol obtained from the above potassium salts by decomposition with dilute nitric acid, is of a pure white colour when freshly precipitated; it is very insoluble in water.

·3599 grm. gave 4535 grm.  $AgBr$ .

	Theory.	I.
$Br_2$ ....	53·87	53·62

(b.) *Dinitrobromophenol*,  $C_6H_2Br(NO_2)_2OH$ . (melting point  $117^\circ$ ).—This body, the main product of the action of nitric acid (sp. gr. 1·42) on dibromophenolparasulphonic acid at somewhat elevated temperatures ( $50^\circ$ — $80^\circ$ ), crystallises from boiling water, in which, however, it is only slightly soluble, on cooling, in short, fine, almost colourless needles.

·3299 grm. gave 2383 grm.  $AgBr$ .

\* Experiments are in progress to determine the amount of gas evolved, and its composition.

	Theory.	I.
Br ....	30.41	30.73

*Potassium Derivative*,  $C_6H_2Br(NO_2)_2OK + Aq.$  — Brilliant yellow, flat needles moderately soluble in hot, difficultly soluble in cold water.

1.0865 grm. lost .0597 grm.  $OH_2$  at  $140^\circ$ .

.4729 grm. thus dried gave .1357 grm.  $K_2SO_4$ .

	Theory.	I.
$H_2O$ ....	5.6	5.49
K.....	12.95	12.88

*Barium Derivative*  $(C_6H_2Br(NO_2)_2O)_2Ba + 4 - 5aq.$  — This salt is very difficultly soluble in cold water. It crystallises in short needles of a more or less deep yellow colour, according to the state of concentration and temperature of the solution from which it separates; this difference in colour corresponds to a difference in the amount of water of crystallisation, thus one sample was found to lose 11.3 per cent. of water on drying at  $180^\circ$ , whilst a second, darker coloured sample lost only 10.18 per cent. By calculation, a loss of 9.8 per cent. corresponds to 4 molecules, a loss of 11.9 per cent. to 5 molecules.

*Calcium Derivative*  $(C_6H_2Br(NO_2)_2O)_2Ca + 7 - 8aq.$  — The salt containing 7 molecules of water separates from a hot concentrated solution on cooling in brilliant, deep orange-coloured, rhombic plates; the filtrate from these crystals deposits the second salt in the form of short, yellow needles, difficultly soluble in cold water. If the first salt be allowed to remain in the solution, it is gradually converted into the second; indeed the tendency to undergo this change is so great, that it is extremely difficult to obtain the former in a state of purity. A sample rapidly dried between folds of bibulous paper lost 18.2 per cent.  $H_2O$  on drying at  $180^\circ$ ; a second similarly prepared, lost 18.4 per cent. The calculated loss corresponding to 7 molecules is 18.2 per cent.; to 8 molecules 20.3 per cent. A quantity of the yellow salt lost 20.3 per cent. of  $H_2O$  at  $180^\circ$ . The above-described behaviour is peculiarly characteristic, and may be employed with great advantage as a means of recognising the presence of the dinitrobromophenol in question.

The action of bromine on ordinary dinitrophenol has already been studied by Laurent (*Kekulé's Lehrbuch.*, iii, 56): he obtained a bromo-dinitrophenol melting at  $110^\circ$ . We have repeated his experiments, and can confirm his observations, with the one exception that we find the melting point to be  $117^\circ$ . The bromodinitrophenol thus prepared is identical in all particulars with the above described; the calcium salts of the two products behave in exactly the same manner.

Dinitrophenol was digested with an excess of bromine in a retort on

the water-bath so long as hydrobromic acid was evolved; the excess of bromine was then distilled off, and the product purified by recrystallisation of its potassium salt.

The purified salt gave the following numbers on analysis:—

·9552 grm. lost ·0532 grm.  $\text{OH}_2$  at  $140^\circ$   
 ·3078 grm. thus dried gave ·0887 grm.  $\text{K}_2\text{SO}_4$ .

	Theory.	I.
$\text{H}_2\text{O}$ ....	5·6	5·5
K.....	12·95	12·93

The phenol obtained by decomposition of this salt with dilute nitric acid exhibited the constant melting point of  $117^\circ$ — $117\cdot5^\circ$ .

·570 grm. gave ·4055 grm. AgBr.

	Theory.	I.
Br ....	30·41	30·27

A barium salt prepared from it lost 10·18 per cent. of water at  $180^\circ$ . Of the two calcium salts obtained, a quantity of the yellow (second) salt lost 20·1 per cent. of water on drying; the orange salt on one occasion was very rapidly dried by pressing between folds of paper, and lost only 16·05 per cent. of water on heating; other specimens lost from 18 to 19 per cent. This would seem to render it probable that the orange salt, when it first separates from the solution, contains less than 7 molecules of water.

(c.) *Dibromonitrophenol*,  $\text{C}_6\text{H}_2\text{Br}_2\text{NO}_2\text{OH}$  (melting point  $117\cdot5^\circ$ ).—This body was always obtained in relatively the same, though small proportion, whatever the conditions of temperature, and the strength of acid employed. It is identical with the product of the direct action of nitric acid on ordinary dibromophenol. We are therefore led to conclude, as in the case (this *Journal*, ix, 1120) of the corresponding dichloronitrophenol (melting point  $125^\circ$ ) obtained by nitration of dichlorophenol-sulphonic acid, that it is formed from a small quantity of dibromophenolmetasulphonate. If this be so, it is evident that the phenol-sulphonic acid employed contained a certain quantity of phenolmetasulphonic acid, the which, notwithstanding the long continued heating, had escaped conversion into the isomeric para-acid.

The following analysis of the above nitro-product was made:—

·3935 grm. gave ·4948 grm. Ag Br.

	Theory.	I.
Br ....	53·87	53·50

The potassium derivative crystallises in anhydrous crimson needles, which exhibit, more especially when seen floating in the solution, a magnificent metallic green lustre.



(d.) *α-Bromonitrophenolsulphonic Acid*,  $C_6H_4BrNO_2OH(SO_3H)$ .

The mono-potassium salt of this acid crystallises in flat, yellow, silky needles, very soluble in hot water, moderately soluble in cold. It is anhydrous.

·4396 grm. gave ·335 grm.  $BaSO_4$  and ·278 grm.  $AgBr$ .

	Theory.	I.
S.....	10·73	10·46
Br ....	26·84	26·91

The dipotassium salt, which crystallises in orange plates, is extremely soluble even in cold water.

*β-Bromonitrophenolsulphonic Acid*,  $C_6H_4BrNO_2OH(SO_3H)$ .

On one occasion, on converting the total nitro-product obtained by the action of nitric acid at  $0^\circ$  on a quantity of 100 grms. of potassium dibromophenolsulphonate into potassium salts, a small residue (about 2 grms.) remained on the filter through which the solution was passed. This was first exhausted with alcohol, by which, however, but little was extracted, and then with boiling water, in which the greater part dissolved. The solution assumed a deep red colour on the addition of potassium carbonate, and carbonic anhydride was set free; on evaporating to a small bulk, and allowing to stand, a crystallisation of brilliant red needles was obtained. The latter dissolved in water gave, on the addition of acetic acid, a precipitate of short yellow needles, which are the monopotassium salt of an isomeric bromonitrophenolsulphonic acid.

Several suppositions may be made as to the origin of this body: either it is formed from the dibromophenolparasulphonate, from which the isomeric *α*-compound is undoubtedly derived, or from the isomeric dibromophenolmetasulphonate; or it owes its origin, and we are inclined to consider this the most probable, to the presence of a small quantity of a potassium monobromophenolsulphonate.

In his paper on the nitrochlorophenols, Petersen (*Ann. Chem. Pharm.*, clvii, 182) discusses the relations between the melting points of corresponding chlorinated and brominated nitrophenols, and comes to the conclusion that the melting points of the former are from  $3^\circ$  to  $4^\circ$  higher than those of the latter.

He compares Laurent's bromodinitrophenol (m. p.  $110^\circ$ ) with a chlorodinitrophenol melting at  $114^\circ$ . Faust's experiments and our own prove, however, that it corresponds to the chlorodinitrophenol melting at  $110^\circ$ — $111^\circ$ , and we have also shown in the above that  $117^\circ$  (approximately) is the true melting point.

Petersen also takes the melting point of dibromorthonitrophenol as at  $141^\circ$ , whereas we believe it to be much lower ( $132^\circ$ ).

The supposed relation, therefore, does not exist, as will be evident from the following comparison :—

<i>Derivatives of Orthonitrophenol.</i>		<i>Derivatives of Nitrophenol.</i>	
Bromorthonitrophenol .....	102°	Bromonitrophenol.....	88°
Chlororthonitrophenol .....	109°	Chloronitrophenol.....	86·5°
	<hr/> — 7° <hr/>		<hr/> + 1·5° <hr/>
Dibromorthonitrophenol .....	132°	Dibromonitrophenol.....	117·5°
Dichlororthonitrophenol .....	125°	Dichloronitrophenol.....	121·5°
	<hr/> + 7° <hr/>		<hr/> — 4·0° <hr/>
Nitrobromorthonitrophenol ....	117°	Nitrobromonitrophenol.....	78°
Nitrochlororthonitrophenol ....	110·5°	Nitrochloronitrophenol.....	80·5°
	<hr/> + 6·5° <hr/>		<hr/> — 2·5° <hr/>

There is an evident relation, however, between the melting points of corresponding chloro- and bromo- phenols *derived from the same parent compound*, which indeed appears extremely probable on a *priori* grounds. More than this cannot be said, since the above numbers are but approximate. We hope, by extending our experiments, to obtain further evidence as to the nature of the relation.

#### VI.—On Bromophenoldisulphonic Acid: its behaviour towards Nitric Acid and Bromine.

By HENRY E. ARMSTRONG.

EXPERIMENT shows, as indeed appeared probable from the beginning, that the first action of bromine on phenoldisulphonic acid is to substitute hydrogen, and so to form a monobromophenoldisulphonic acid, which by the further action of bromine is converted successively into dibromophenolsulphonic acid and into tribromophenol.

In preparing potassium phenoldisulphonate, the slight modification of Kekulé's method described by Engelhardt and Latschinoff (*Zeitschr. f. Chem.* [2], iv, 270) was adopted.

*Action of Bromine.*—A cold moderately dilute solution of potassium phenoldisulphonate was treated with bromine in the proportion requisite to form the monobrominated derivative: the solution is at first coloured yellow, but the bromine disappears rapidly on shaking. After standing for some hours, crystals are deposited, and a further quantity is obtained on evaporating the solution.

That the product is the expected potassium bromophenoldisulphonate is shown by the following analysis:—

·3196 grm. gave ·1477 grm. AgBr and ·397 grm. BaSO<sub>4</sub>.

·2406 grm. gave ·0994 grm. K<sub>2</sub>SO<sub>4</sub>.

	Theory.	I.
Br . . . .	19·55	19·66
S . . . . .	15·64	17·05
K . . . . .	19·07	18·49

This salt is very soluble in hot, and moderately soluble in cold water. Barium chloride produces no precipitate with it, except in very concentrated solutions. It crystallises either in needles or in tufts of short flat blades, which rapidly disintegrate to a snow-white anhydrous powder on exposure to the air.

It is violently acted upon by nitric acid (sp. gr. 1·36) and unless precaution be taken, is for the greater part converted into trinitrophenol. By gradually adding the dry salt to the well cooled acid, it is converted into bromodinitrophenol, identical with the product of the action of bromine on dinitrophenol, as was proved by the identity of melting point (117°) and crystalline form of the phenols from the two sources; by the appearance of the potassium derivative; and more especially by the characteristic separation of the calcium derivative from a hot saturated solution in orange coloured rhombic plates, and from the cold dilute solution in yellow needles.

·3429 grm. gave ·2456 grm. AgBr.

	Theory.	I.
Br . . . .	30·41	30·47

By the action of carefully cooled nitric acid somewhat less concentrated than the above, the bromophenoldisulphonate is only partially converted into bromodinitrophenol; a considerable portion is so acted upon that KSO<sub>3</sub> is replaced by NO<sub>2</sub>, thus forming a potassium bromonitrophenolsulphonate. This is readily separated, after removing the excess of nitric acid by filtration and washing on a vacuum-filter with cold water, by digesting the mixed product with hot water, which dissolves the sulpho-salt and but very little bromodinitrophenol. It crystallises in short pale yellow needles, quite different in appearance from the potassium  $\alpha$ -bromonitrophenolsulphonate obtained by nitration of potassium dibromophenolparasulphonate. It is also, I believe, *isomeric* with the potassium  $\beta$ -bromonitrophenolsulphonate, and may therefore be termed provisionally potassium  $\gamma$ -bromonitrophenolsulphonate.

A complete analysis of this salt was not made. Judging from the bromine and sulphur determinations, however, it contains one molecule of water of crystallisation—



·3675 grm. gave ·2182 grm. AgBr and ·259 grm. BaSO<sub>4</sub>.

	$\text{C}_6\text{H}_2\text{BrNO}_2\text{OH}(\text{SO}_3\text{K}) + \text{aq.}$	I.
Br . . . .	25·31	25·26
S. . . . .	10·12	9·67

The dipotassium salt crystallises in short bright-red needles.

A small quantity of a dibromonitrophenol (melting point 117·5°) yielding a deep red potassium derivative was always obtained, together with the above-mentioned nitro-products. The formation of this body appeared to show that potassium bromophenoldisulphonate was converted by the further action of bromine into potassium dibromophenolsulphonate.

This proves on examination to be the case. A weighed quantity (409 parts) of pure potassium bromophenoldisulphonate was dissolved in water, and the well cooled solution treated with bromine (160 parts) which disappeared rapidly on shaking. On standing, a small quantity of *tribromophenol* separated; this was removed by filtration, the solution evaporated to dryness, and the residue at once acted upon by nitric acid. The nitro-product consisted chiefly of dibromonitrophenol (melting point, 117°·5) yielding the characteristic red potassium salt, together with a small quantity of dinitrobromophenol (melting point, 117°), evidently the nitro-product of the bromodisulpho-salt which, owing to the formation of some tribromophenol, had escaped the action of bromine.

In the previous communication the conclusion has been drawn that the dibromonitrophenol in question is the nitration-product of dibromophenol*metasulphonic* acid; consequently the above observation shows that bromophenoldisulphonic acid is converted into dibromophenol*metasulphonic* acid by the action of bromine, and it is therefore probable that the potassium  $\gamma$ -bromonitrophenolsulphonate above described is also a *phenolmetasulphonic* acid derivative.

Many instances are known of the conversion of isomeric substitution-compounds into the same higher substitution-compounds by the action of the same agent; and it may fairly be asked, can no rule be given which shall enable us to predict the nature of the product which results when in such a case the higher substitution-compound is submitted to a reverse action, and is reduced to the lower—will the compound C, into which the isomeric bodies A and B are alike convertible, yield A or B when reconverted?

Although we have comparatively little evidence on this point, all that which we possess tends, I believe, in the same direction, as shown by the following examples:—

1. On nitration of toluene, two isomeric mononitrotoluenes are

obtained, viz., *orthonitrotoluene*\* (liquid) and *paranitrotoluene* (melting point,  $54^{\circ}$ ), both of which yield the same dinitrotoluene on further nitration. By partially reducing this dinitrotoluene with ammonium sulphide, converting the nitrate of the amidonitrotoluene into diazonitrotoluene nitrate, and acting upon this by absolute alcohol, it is reconverted into *orthonitrotoluene* (Beilstein and Kuhlberg, *Ann. Chem. Pharm.*, clv, 13).

2. The two modifications of nitrophenol, *orthonitrophenol* (melting point,  $110^{\circ}$ ) and *metanitrophenol* (melting point,  $45^{\circ}$ ) are convertible into the same dinitrophenol; if this be reduced to amidonitrophenol, and the diazonitrophenol obtained from the latter be acted upon by hydriodic acid, an idonitrophenol is produced, identical with the product of the action of iodine on *orthonitrophenol* (Körner, *Zeitschr. f. Chem.* [2] iv, 324).

3. Dinitrophenol and chlorine give chlorodinitrophenol (melting point,  $110^{\circ}$ – $111^{\circ}$ ), from which, by the above series (Example 2) of reactions,  $\text{NO}_2$  may be removed and replaced by H; the chloronitrophenol thus obtained is identical with the product of the action of chlorine on *orthonitrophenol*. (Faust, this *Journal* [2] x, 62; Armstrong, *ibid.* x, 14).

If the existence of three series of isomeric di-derivatives of benzene—and of isomerides generally—be regarded as a consequence of the expenditure of different amounts of force in the reactions by which the isomerides are formed, and if for the nonce it be assumed that least force is expended in the formation of compounds of the ortho-series, the greatest amount in that of para-derivatives, and an intermediate amount in the case of meta-derivatives, or, in other words, that the so-called ortho-derivatives are bodies of higher potential energy than either the corresponding meta- or para-derivatives, then the above quoted reactions appear to show that, given a compound C, capable of being formed from either of two isomerides A and B, this compound C will be reconverted on reduction into the body A, if A be an ortho- and B a meta- or para-derivative, or if A be a meta- and B a para-derivative: that is to say, that the body A will be obtained on reduction if in the formation of A less force has been expended than in the formation of B.†

The conversion of bromophenoldisulphonic acid into dibromophenol-metasulphonic acid previously described is obviously in accordance with

\* Usually termed *metanitrotoluene*; v. Meyer's experiments (*Ann. Chem. Pharm.*, clvi, 265, and cliv, 1), show, however, that the so-called meta-derivatives of toluene are really members of the phthalic acid, or *ortho*-series. Compare also Fittig, *Zeitschr. f. Chem.* [2], vii, 179 and 587.

† I propose to discuss this subject, and my reasons for adopting the above explanation of isomerism, fully in a future communication, so soon as a series of experiments bearing on the question are completed.

this statement. The conditions under which phenol is converted into phenolmeta- and phenolpara-sulphonic acids show that there is a greater expenditure of force in the formation of the latter.

Two classes of reactions only have been discussed in the foregoing: the reduction of nitro-compounds by Griess's method, and the reduction of sulpho-acids by bromine; it is possible that in other classes of reactions, the relation, if that above pointed out be not apparent only, may be of a different order.

It is hoped that the further investigation of the disulpho-acids will lead to useful results bearing on this question. I propose in the first place to examine the phenoldisulphonic acid which, according to Mr. Duppa, is obtained by heating salicylic acid with an excess of sulphuric acid to 180°.

My acknowledgment is due to my friend Mr. Elltoft, for the manner in which he has interested himself in preparing many of the above described compounds.

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## VII.—On the Formation of Substituted Nitrophenolsulphonic Acids.

By HENRY E. ARMSTRONG and FRED. D. BROWN.

ALL attempts to convert the chlorinated nitrophenols by double decomposition with ammonia, &c., into compounds of other series having proved unsuccessful, we were induced to commence the examination of corresponding iodo-compounds, on the assumption warranted by general experience, that they would prove more manageable bodies. Moreover, our knowledge of the idonitrophenols is almost *nil*, so that considerable interest attaches to their examination on this account alone. A third and indeed chief motive which urged us to make the investigation was to compare the action of iodine with that of chlorine and bromine, and the iodophenol-derivatives generally with the better known chlorinated and brominated compounds.

It appears highly probable that, at least in some instances, iodine which has a so much lower reactive energy than either chlorine or bromine, will differ considerably in its action from either of the latter, indeed the experiments of Körner (*Zeitschr. f. Chem.* [2], iv, 322), and those of Hlasiwetz and Weselsky (*Deut. Chem. Ges. Ber.*, ii, 522) already furnish evidence of the anomalous behaviour of iodine; thus by its action on phenol in presence of iodic acid (in aqueous solution) according to the former observer, a mixture of ortho- and meta-iodophenols is formed, whereas Hlasiwetz and Weselsky state that in presence of mercuric oxide (and in alcoholic solution) the chief product is paraiodophenol.



At the commencement of our experiments in this direction we were so fortunate as to make certain observations which, although they have for the moment somewhat diverted our attention from the main object in view, possess considerable interest as showing the influence of change of condition on the course of chemical action.

It has been shown by Schmidt and Glutz (*Deut. Chem. Ges. Ber.*, ii, 51) that when a current of chlorine is passed into an aqueous solution of sodium nitrophenolsulphonate dichlorónitrophenol (melting point  $121.5^{\circ}$ ) is produced.

Substituting bromine for chlorine we have obtained analogous results: a yellow precipitate is at once thrown down on the addition of bromine to an aqueous solution of potassium nitrophenolsulphonate, consisting of the corresponding dibromonitrophenol (melting point  $117.5^{\circ}$ ), identical with the product of the action of nitric acid on ordinary dibromophenol.

·5400 grm. gave ·6849 grm. AgBr.

	Theory.	I.
Br . . . .	53.87	53.97

We expected, therefore, that iodine would yield the corresponding di-iodonitrophenol; but thinking that its insolubility in water would militate against the success of the experiment, an alcoholic solution of nitrophenolsulphonic acid\* was employed. In order, however, to withdraw the hydriodic acid formed from the sphere of action, Hlasiwetz and Weselsky's method was adopted, and after each addition of iodine a small quantity of dry, finely powdered mercuric oxide was introduced.

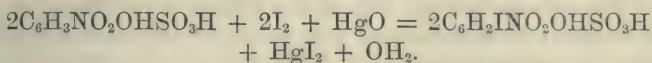
The iodine disappeared slowly on agitation, and the solution became perceptibly warm, but after an amount slightly in excess of that required by the proportion,  $I_2 : C_6H_3.NO_2.OH.SO_3H$ , had been added, the colour communicated to the solution by the iodine ceased to disappear on shaking. On distilling off the alcohol in the water-bath, after removing the mercuric iodide and excess of mercuric oxide by filtration, a small quantity of iodine passed over with it. The addition of water to the residue caused the separation of traces of a brown crystalline substance, which proved to be a mixture of iodine and di-iodonitrophenol. On treating the filtrate with potassium carbonate, pale yellow crystalline scales, much resembling chloranil in appearance, separated out to such an extent that the solution became almost solid. These were collected on a vacuum filter, recrystallised from hot water, dried at  $100^{\circ}$ , and analysed.

\* Prepared by acting upon volatile nitrophenol with  $SO_3HCl$ . This *Journal*, ix, 175.

·5427 grm. gave ·3319 grm. AgI, and ·3456 grm. BaSO<sub>4</sub>.  
 ·4665 grm. gave ·1047 grm. K<sub>2</sub>SO<sub>4</sub>.  
 ·3369 grm. gave ·0762 grm. K<sub>2</sub>SO<sub>4</sub>.

	C <sub>6</sub> H <sub>2</sub> INO <sub>2</sub> OHSO <sub>3</sub> K.	I.	II.
I. ....	33·15	33·05	—
S ....	8·35	8·77	—
K ....	10·20	10·07	10·15

The action of iodine, therefore, on an alcoholic solution of nitrophenolsulphonic acid in presence of mercuric oxide gives rise to the formation of an idonitrophenolsulphonic acid, according to the equation:—



The above potassium salt is readily soluble in boiling water, but slightly soluble in cold water; it crystallises in short fine needles, united in groups; the air-dried salt is anhydrous. It dissolves in a solution of potassium carbonate with effervescence, forming a deep red-yellow liquid, from which the dipotassium salt may be obtained on evaporation. This salt when finely divided has a bright red colour, but the larger crystals obtained on allowing a solution to evaporate spontaneously are of a very deep red colour, and consist apparently of rhombic prisms. These crystals are anhydrous.

·7825 grm. gave ·3283 grm. K<sub>2</sub>SO<sub>4</sub>:—

	Theory.	I.
K. ....	18·56	18·83

On the addition of barium chloride to a moderately dilute solution of the mono-potassium salt, barium idonitrophenolsulphonate is precipitated in the form of pale-yellow, silky needles, containing four molecules of water of crystallisation.

·8428 grm. lost ·0576 grm. H<sub>2</sub>O at 180°:—

	Theory.	I.
4H <sub>2</sub> O. ....	7·3	6·83

On exposure to the air, this salt loses its lustre, evidently owing to loss of water of crystallisation.

The action of iodine on an aqueous solution of nitrophenolsulphonic acid also gives rise to the formation of mono-idonitrophenolsulphonic acid, but owing to the insolubility of iodine in water, the reaction takes place with extreme slowness. As in the former experiment mere traces only of di-idonitrophenol were produced, and there would seem to be little tendency to form this compound, even by the action of an excess of iodine either in alcoholic or in aqueous solution.

Before the action of iodine in aqueous solution had been examined, it was thought that perhaps the employment of alcohol as solvent had influenced the formation of the moniodo-compound, and preliminary experiments as to the action of chlorine and bromine under like conditions were instituted in order to obtain evidence on this point.

The results show that, although in the case of iodine the solvent simply influences the rate of action by increasing the solubility of the iodine, this solvent does exercise an influence on the course of the action when chlorine or bromine are the agents.

By acting upon carefully cooled alcoholic solutions of nitrophenol-sulphonic acid with bromine and chlorine respectively, we have succeeded in obtaining monobromo- and monochloronitrophenolsulphonic acids. The monopotassium salt of the former crystallises in pale-yellow needles; its di-potassium salt in bright-red needles closely resembling the corresponding salt of the  $\gamma$ -bromonitrophenolsulphonic acid, described in the previous communication.

The chloronitrophenolsulphonic acid is isomeric with the similar compound formed by nitration of dichlorophenolparasulphonic acid (this *Journal*, ix, 1118); its dipotassium salt forms small orange-yellow, sharply defined prismatic needles totally different from the corresponding salt of the latter acid.

At present we have not yet examined these bodies in detail, but propose to do so. Their formation shows clearly, however, that the formation of dichloro- or dibromo-nitrophenol from an aqueous solution of nitrophenolsulphonic acid by the action of chlorine or bromine, is preceded by that of monochloro- and monobromo-nitrophenolsulphonic acids.

It is well known that anthracene cannot be nitrated by the action of aqueous nitric acid, whereas by Bolley's method of nitration in alcoholic solution, it readily yields mono- and di-nitroanthracene. Similarly by acting upon an alcoholic solution of  $\beta$ -naphthol by nitric acid, Wallach and Wichelhaus (*Deut. Chem. Ges. Ber.*, iii, 846) were able to obtain dinitro- $\beta$ -naphthol, all other methods having failed. Again, Griess has shown (*Ann. Chem. Pharm.*, cliv, 202) that an aqueous solution of ammonium trinitrophenol is easily reduced to diamidonitrophenol, whereas in alcoholic solution the reduction stops so soon as amidodinitrophenol is formed. All these are instances parallel with the above, and show clearly the influence which change of condition has on the course of chemical change.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
BRITISH AND FOREIGN JOURNALS.

**Physical Chemistry.**

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**The Primary Spectrum of Iodine.** By G. SALET (Compt. rend., lxxv, 76).

By employing tubes, "à gâines," the author, by means of a current of weak tension, has succeeded in obtaining the primary spectrum of iodine exactly corresponding to the absorption spectrum of this element. Being especially developed in the blue and indigo, the colours which stand nearest to the characteristic colour of iodine, this spectrum can scarcely be attributed to the presence of an impurity. It seems therefore to afford a strong argument in favour of Pluecker's theory of "multiple spectra."

R. S.

**Effects of Slow Actions prolonged for a number of Years.**  
By BECQUEREL (Compt. rend., lxxv, 52).

METALLIC, alkaline, and acid solutions were allowed to act upon each other for a number of years, being brought into direct contact within hermetically sealed glass vessels, or separated from each other by cracked tubes, or by porous earthenware.

When solutions of gold and of potassium plumbate were made to act upon each other in an electro-capillary apparatus, metallic gold was deposited on one side and red lead on the other side of the partition.

Among the products formed within hermetically sealed vessels, opened only after the lapse of twenty years, the most remarkable were:—(1.) Arragonite crystals, by contact of gypsum with solution of potassium bicarbonate. (2.) Rhombohedral crystals of calcium carbonate, by contact of gypsum with sodium carbonate. (3.) Crystals of calcium arsenite, almost as beautiful as those found in nature. (4.) Crystals of the double sulphate of calcium and potassium, by contact of potassium aluminate with gypsum. (5.) Crystals of lead carbonate, by contact of pieces of galena with potassium bicarbonate. (6.) Crystalline scales of hydrated lead carbonate, by contact of calcespar and potassium plumbate.

On immersing porous plates of calcespar, 1 centimeter thick, into a solution of cupric nitrate, and transferring them, with the cuprous nitrate formed within them, into a solution of potassium bicarbonate, it was found that the plates, without having changed their structure, were converted into malachite. In order to allow the solutions to penetrate thoroughly into the interior of the plates, the carbonic acid and liquid compounds formed had to be removed from the pores by operating *in vacuo*.

R. S.

**Theory of the Explosion of Detonating Compounds.** By P. CHAMPION and H. PELLET (*Compt. rend.*, lxxv, 110—114).

THIS paper describes a series of experiments undertaken with the object of following out Abel's theory, that for the explosion of detonating compounds a certain kind of mechanical excitement is necessary, the nature of which depends on the nature of the compound itself. The experiments made tend to show that at least in certain cases the heat and the shock of an explosion at a distance operate in producing a second explosion only by producing a certain vibratory motion, which is obtainable by other means.

The first experiments tried were on explosions produced by means of a previous explosion at a distance. The detonator employed was iodide of nitrogen, which the authors found particularly suitable for delicate experiments. A tube, at first over two meters, and afterwards seven metres long, was constructed of two lengths joined together by a paper band. Small quantities of the iodide were placed at each end, and it was found that an explosion produced at one end of the tube immediately caused the explosion of the iodide at the other end. To determine whether the second explosion was caused by the pressure of the air in the tube due to the sudden production of gas by the first explosion, a light pith ball pendulum was suspended within the tube, and trials with this indicator completely negatived the idea that this was possible. If in the experiments described the tubes are not joined together by the paper band, but separated by an interval of five or six millimeters, the second explosion is not produced, or can only be obtained by using a comparatively large quantity of the iodide for the first explosion.

After this, experiments were tried on producing explosion by means of other kinds of excitement. Iodide of nitrogen was fastened by means of a morsel of gold-beater's skin to the strings of a thorough-bass violin. It was found, on bowing the strings, that the iodide which was placed on the two lower strings did not explode, while that placed on the string giving the highest note exploded instantly on being touched with the bow. On trial it was found that the lowest number of vibrations that would produce an explosion was about 60\* per second.

Experiments were also made with the vibrations of metallic plates and with two small Chinese gongs. The result was the same. Vibrations that gave deep sounds had no effect; but those giving the higher sounds readily produced an explosion.

The experiments above described illustrate the effect of vibrations in causing explosion of a detonator. The following show that heat, unless it is accompanied with mechanical vibrations of the proper kind, does not produce explosion with readiness.

Iodide of nitrogen was placed at the focus of a parabolic mirror, and at the focus of a second similar mirror, nitroglycerin, fulminate of mercury, and gunpowder were exploded. The quantity of nitroglycerin necessary to cause the explosion of the iodide of nitrogen in the other

\* According to ordinary English reckoning, 30 per sec. The French count half vibrations instead of complete vibrations from one end of the range to the other, and back again.—J. T. B.

focus was determined; and it was found that as much powder was required as would produce ten times the heat given out in the burning of the required quantity of nitroglycerin. The mirrors were afterwards covered with lamp-black, and then even this large quantity of powder would not cause the iodide of nitrogen to explode. On the other hand, the lamp-black covering did not in the least prevent the nitroglycerin in one focus from exploding the iodide of nitrogen in the other.

From these experiments the authors conclude that the cause of the explosions of detonants produced by influence is generally a kind of vibratory motion, and that the nature of the motion necessary depends upon the nature of the explosive.

J. T. B.

**A New Sensitive Singing Flame.** By W. E. GEYER (*Am. J. of Sci.* [3], iii, 340—342).

MR. GEYER describes a method of modifying the sensitive flame of Mr. Bang, mentioned in *Nature*, Nov. 2, 1871. Mr. Bang places a piece of wire gauze four inches above a very fine burner, and lights the gas above the gauze. He thus produces a very sensitive flame. Mr. Geyer adds to this a tube which rests upon the gauze, and encloses the flame. By altering the distance of the tube and gauze from the burner, a flame of extraordinary sensitiveness is obtained. It may also be made by proper adjustment either to roar continuously, or to roar when excited by external noises, or it may be merely a silent sensitive flame.

J. T. B.

**Constitution of Acid Salts in Solution.** By M. BERTHELOT (*Compt. rend.*, lxxv, 207—210, and 263—267).

It is generally supposed that an acid salt or a double salt is broken up in the act of solution in water, and that the components, the neutral salt and the free acid, or the two salts, remain in the solution side by side, but uncombined. The experiments of Andrews, Graham, and Favre and Silberman, on heat of combination, are relied on in proof of this assertion. On carefully examining the question, however, Berthelot finds a difference in this respect between the salts of monobasic and of bibasic acids. Acid salts of the monobasic acids, he finds, are really completely decomposed during solution, but acid salts of the bibasic acids are only partially broken up, and that to an extent which depends upon the relative proportions of the neutral salt, the acid, and the water present.

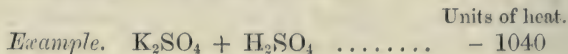
Berthelot's experiments were the following:—The salts of potassium, sodium, and ammonium, with hydrochloric acid and with nitric acid, were dissolved. The strength of the solutions was such that two litres contained an equivalent of the salt in grams. Similar solutions of the two acids were made. With the solution of each salt was mixed an equal volume of the solution of the acid proper to it, and the change of temperature was observed. In these cases the heat absorbed or disengaged was scarcely perceptible, and scarcely greater than that allowed for experimental errors.



Thus for the salts of potassium—



Similar experiments were then tried with the alkaline salts of sulphuric acid and oxalic acid in solution, whose strength was half an equivalent in grams to two litres of water.



On mixing the solution of the other salts with the acid solution similar quantities of heat were absorbed. Such figures indicate a decided reaction between the neutral and the acid salt.

To examine the nature of this reaction, different quantities of acid solution were successively added to solutions of potassium sulphate, and the heat absorbed was observed. Thus there were in solution successively K<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub> + 2H<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub> + 10H<sub>2</sub>SO<sub>4</sub>; and it was found that the quantity of heat absorbed became greater as the quantity of acid added was greater, but that it had a limiting value, about 2,000 units of heat, a quantity which may be looked upon as that which represents a complete transformation of the neutral into the acid sulphate. Similar results were obtained with oxalate of sodium.

Again experiments were made by adding to solutions containing one equivalent of sulphuric acid, one, two, or more equivalents of neutral potassium sulphate. The result was similar to that just described, reactions being obtained which approached more and more closely to that which would correspond to complete conversion of the sulphuric acid into the acid sulphate of potassium. Oxalic acid gave a similar result with neutral oxalate of sodium. The limiting value for the quantity of heat absorbed in these last experiments, a value which may be supposed to belong to a complete conversion of an equivalent of sulphuric acid into acid sulphate of potassium by means of the presence of a large quantity of neutral sulphate, or of an equivalent of oxalic acid into acid oxalate of sodium by means of neutral oxalate, was the same as that found for the converse reaction, being 2,000 units of heat for the sulphate of potassium, and 600 units for the oxalate of sodium; and it is interesting and important to remark that the heat given out during the conversion, by means of potash, of sulphuric acid into potassium sulphate, viz., 15,700 units, when reduced by this number 2,000, gives 13,700 units, the same quantity that is given out during the conversion of a monobasic acid, such as nitric or hydrochloric acid by the same means. A similar comparison for the case of sodium oxalate may be made.

Lastly, experiments were tried as to the effect of the water of solution, and it was found that on mixing an equivalent of sulphuric acid with an equivalent of a neutral potassium sulphate, first each dissolved in one litre of water, then each in two, afterwards each in five litres, and so on, the quantity of heat absorbed became less and less. This

\* The unit of heat is the quantity of heat required to raise 1 gram of water 1° C.

represents a reaction less and less complete, as the solution is more and more dilute. In a solution in which one equivalent of this double salt is contained is 20 litres of water, little more than the half will remain as a double salt, the remainder being split up into free acid and neutral sulphate.

These facts concur in showing that there is a species of equilibrium by means of which, in the case of the salt of a bibasic acid, the four bodies, the water, the double salt, the free acid, and the neutral salt, all coexist in the same solution. The proportion in which they coexist depends upon the proportions of water, acid, and neutral salt present.

The formation of a bisulphate by solution is accompanied by an absorption of heat. Berthelot examines into the cause of this, and shows that during the formation of the bisulphate heat is really given out, and that the apparent absorption of heat is due to secondary phenomena connected with the solution of the salt in water, which, taken together, overpower the dominant phenomenon, viz., the formation of the salt. His investigations were made upon potassium bisulphate.

He first determines the quantity of heat absorbed when an equivalent of potassium sulphate ( $K_2SO_4$ ) is dissolved in various quantities of water. He then determines the quantity of heat absorbed during the solution of an equivalent of potassium bisulphate under various circumstances. He finds also the quantity absorbed when the bisulphate is formed by solution. Thus  $\frac{1}{2}$  eq.  $H_2SO_4$  in 2 litres of water, mixed with  $\frac{1}{2}$  eq. of  $K_2SO_4$  in 2 litres of water, absorb 1040 units of heat; the experiment being made between  $22^\circ$  and  $24^\circ$  C. According to experiments by Thomsen, on mixing  $\frac{1}{2}$  eq. of sulphuric acid with two litres of water ( $\frac{1}{2}H_2SO_4 + 110H_2O$ ), 8,540 units of heat are given out. From these data, Berthelot made a calculation of the quantity of heat given out in the formation of potassium bisulphate.

Let us have initially solution of sulphuric acid  $\frac{1}{2}$  eq. in 2 litres, and solution of potassium sulphate ( $K_2SO_4$ ),  $\frac{1}{2}$  eq. in 2 litres; and let us obtain finally potassium bisulphate,  $K_2SO_4 + H_2SO_4 = 2KHSO_4$ , 1 eq. in 4 litres of water. This result may be imagined to be arrived at in two different methods. Their heat-relations are as follows:—

First method—

	Units of heat.
Mixing the two liquids .....	—1040

Second method—

Separate the sulphuric acid from its solution....	—8540
Separate the potassium sulphate .....	+2980
Combine in anhydrous way $K_2SO_4 + H_2SO_4$ ..	$x$
Dissolve potassium bisulphate .....	—3480

Total.....  $x - 9040 = -1040$

Hence—

$$x = + 8000.$$

8,000 units is then shown to be the quantity of heat given out during the combination of potassium sulphate and sulphuric acid to form potassium bisulphate. A similar calculation, derived from the data

furnished by experiments of Graham, gives for the quantity of heat disengaged in the formation of sodium bisulphate from sodium sulphate and sulphuric acid, 8,200 units.

From the numbers here quoted it is easy to see the reason of the, at first sight, anomalous production of cold during the formation of an alkaline bisulphate by the mixture of the two solutions. The reactions which cause an absorption of heat are the withdrawal of the sulphuric acid from the water in which it was dissolved and the solution of the bisulphate formed. Similar causes, though more complicated, give rise to the extraordinary cooling effect observed when crystallised sodium sulphate is added to dilute sulphuric acid. The absorption of heat due to the separation of the sodium sulphate from its water of crystallisation, must be reckoned in this case with the other causes of diminished temperature.

The remainder of the paper is taken up with an examination of phenomena met with in comparing the hydrated and the anhydrous potassium bisulphate. Berthelot finds that the ordinary method of preparing anhydrous potassium sulphate does not really give that salt. By using 1 or  $1\frac{1}{2}$  eq. of sulphuric acid, that is by crystallising from a solution slightly acid, beautiful needle-like prisms are obtained, which have generally been considered to be anhydrous potassium bisulphate ( $K_2SO_4, SO_3$ ). If, however, the solution be more strongly acid, the hydrated bisulphate is formed. Berthelot shows that the former salt is not really anhydrous potassic bisulphate, but has for its formula  $4K_2SO_4, 3H_2SO_4$ . This being considered as established, the reason of the formation of the true bisulphate from a more acid solution is apparent.

Having prepared real anhydrous potassium bisulphate by acting on dry potassic sulphate with anhydrous sulphuric acid, and melting the salt formed over an oil-bath at  $180^\circ C.$ , he examined it with the following results:—

Immediately on solution considerable depression of temperature is observed, 1,910 units of heat being absorbed when one part of the salt is dissolved in 40 parts of water. But the thermometer soon begins to rise again, and as much as 580 units of heat are given out in five or six minutes. The absorption of heat is due to the solution of the salt in water; the evolution of heat during the second part of the reaction to the combination of the anhydrous bisulphate with the water. The latter reaction is not, however, complete in the time mentioned, for by calculation it is shown that as much as 1,450 units of heat are given out during the conversion of the anhydrous bisulphate into dissolved bisulphate. The reaction is a progressive one, analogous to the conversion of anhydrous into hydrated acetic acid.

To calculate the heat given out during the reaction—



There are two methods, starting from the initial circumstances, *anhydrous acid, and dry sulphate, and water* (about 4 litres), of arriving at the final result, *hydrated bisulphate in solution*.



Units of heat given out.

1.	$\text{SO}_3 + \text{K}_2\text{SO}_4 = \text{K}_2\text{S}_2\text{O}_7$ .....	$x$
	Solution of $\text{K}_2\text{S}_2\text{O}_7$ .....	1450
	Dilution, about. ....	110
	Total. ....	$x + 1560$

2. Reciprocal action between  $\text{SO}_3$  and water, and  $\text{K}_2\text{SO}_4$  and water—

Units of heat given out.

$\text{SO}_3 + \text{water}$ .....	18650
$\text{K}_2\text{SO}_4 + \text{water}$ .....	— 2980
Reaction $\text{H}_2\text{SO}_4 + \text{K}_2\text{SO}_4$ ....	— 1040
Total .....	+ 14630

Hence—

$$x + 1560 = 14630.$$

$$x = 13000.$$

During the hydration of this salt ( $\text{K}_2\text{S}_2\text{O}_7 + \text{H}_2\text{O} = 2\text{KHSO}_4$ ), 5,000 units of heat are given out, which is about half the heat given out during the reaction  $\text{SO}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$ .

J. T. B.

## Inorganic Chemistry.

**Preparation of Ozone by a New Method of Producing a Silent Discharge of Electricity.** By A. BOILLOT (Compt. rend., lxxv, 214).

THE author describes an apparatus for producing a silent discharge of electricity, by means of which he says that he obtains a much larger quantity of ozone in oxygen than by any of the ordinary methods.

The apparatus is constructed as follows:—A tube 32 c.m. long and 14 m.m. in diameter, was covered externally over 29 c.m. of its length with powdered coke, which was caused to adhere by coating the tube thinly with gelatin. Another tube 29 c.m. long, and 8 mm. in diameter, and closed at both ends, was similarly covered with powdered coke, so as to form a cylinder of carbon. This tube could enter completely within the former tube, leaving a space between the two for the passage of a current of oxygen. One of these tubes was connected with one pole of an induction machine, the other tube with the other pole by means of a platinum wire, and the whole was enclosed in an outer tube of glass. With four Bunsen's elements applied to the induction coil, the silent discharge was kept up for several hours without interruption. A current of oxygen flowed through the apparatus during that time, and a large quantity of ozone was obtained.

J. T. B.

**Preparation of Cæsium and Rubidium Salts from Lepidolite**

By L. de BOISBAUDRAN (Bull. Soc. Chim. de Paris [2], xvii, 551).

A SOLUTION containing alkaline salts only is obtained from lepidolite, more rapidly than by the usual methods, by acting on that mineral with hydrofluoric acid, adding excess of chalk, filtering, precipitating with sodium carbonate and sodium sulphide, and again filtering.

In separating the rubidium and cæsium by Bunsen's method, it is better, instead of washing the mixed bitartrates, to dissolve them in just enough hot water, and to stir the solution till it is cold. When the resulting precipitate of rubidium bitartrate is treated in the same way two or three times, it is obtained quite free from cæsium.

B. J. G.

**Reduction of Thallium from the Chloride.** (Ann. Chem. Pharm., clxiv, 74.)

PROFESSOR WOEHLEER recommends for this purpose the fusion of an intimate mixture of 20 parts of thallium chloride, 8 parts of dry soda, and 1 part of lamp-black at a low red heat. There is always a slight loss, however, owing to the volatilization of chloride at the commencement of the operation. This may perhaps be avoided, he suggests, by making the mass into a paste with water, and again drying before fusion.

H. E. A.

**Preparation of Barium, Strontium, and Calcium Peroxides.**

By H. STRUVE (Zeitschr. Anal. Chem., xi, 22—30).

WHEN freshly precipitated barium carbonate is exposed to a low red heat, it loses slightly in weight, and a small quantity of barium peroxide is formed, which, on being treated with water and carbonic anhydride, furnishes hydrogen peroxide. The carbonates of calcium and strontium also yield small quantities of the respective peroxides when heated in contact with air.

A. T.

**Solution of Calcium Carbonate by Carbonic Acid.** By TH.

SCHLOESING (Compt. rend., lxxv, 70—73).

FINDING that the quantity of calcium bicarbonate dissolved in water varies with the slightest changes of the tension of the carbon dioxide in the atmosphere, the author has established by a series of experiments, that the law regulating the amount of bicarbonate dissolved, can be expressed by the formula—

$$x^m = k y,$$

where  $x$  denotes the number of grams of the salt in solution, and  $y$  the tension or pressure of the carbon dioxide in the atmosphere, 760 mm. of mercury being taken as the unit of pressure. The differences between the amounts of dissolved salt actually found at different ten-

sions and those which, according to the above formula, should be dissolved at these same tensions, are so small that, independently of errors of experiment, they may be attributed to the influence of temperature which had unfortunately been allowed to vary between  $15^{\circ}$  and  $16^{\circ}$ , whilst, as the author afterwards found, the variations of the temperature by a single degree would almost wholly account for the discrepancies of the calculated and the experimental results.

By a mathematical transformation, the above law may be expressed as follows: *The values of the tension between certain limits, and the corresponding values of bicarbonate dissolved, form two geometrical progressions with different ratios, the ratio of the first being greater than that of the second progression.*

Whilst for calcium carbonate  $m$  is  $= 0.37866$ , and  $k = 0.92128$ , it was found that for barium carbonate, with regard to which an exactly analogous law holds good,  $m$  is  $= 0.38045$  and  $k = 0.534726$ . It will be seen that the values of  $m$  are almost identical for the two salts.

R. S.

**Iron Phosphides.** By C. FREESE (Deut. Chem. Ges. Ber., v, 604).

THE method adopted by Sidot (*Compt. rend.*, lxxiv, 1425; p. 677 of this volume) for obtaining an iron phosphide,  $\text{Fe}_4\text{P}$ , was shown by the author five years ago to be utterly fallacious, being capable of yielding phosphides of variable composition according to the diameter of the iron wire used. Hence the theory of Maumené is deprived of one of its supports, that theory being partly founded on the production of this phosphide, which according to the author has no existence.

C. R. A. W.

**On the Red Coloration sometimes observed in White Lead.**

By A. BANOW and G. KRAEMER (Deut. Chem. Ges. Ber., v, 545—556).

A NUMBER of carefully analysed samples of commercial lead were converted into white lead by being put into pots covered with boards and spent tan, and containing either wood- or wine- or malt-vinegar or dilute acetic acid.

A red, merely superficial coloration of the product was observed only in some pots in which the free circulation of the air had been interrupted by a species of fungus growing over the edges of the pot and board, and where besides the spent tan had been changed into a caked felt-like-mass less easily disposed to fermentation. This, coupled with the fact that the same kinds of lead which furnished this coloured product yielded perfectly faultless white lead when nothing interfered either with the circulation of the air or with the fermentation, induced the authors to seek the cause of the coloration neither in the impurities of the lead nor in the nature of the vinegar employed, but in some fault of the process giving rise to the formation of a coloured compound of lead with a non-metallic substance. The absence of red lead in the red product obtained by the authors was proved by its complete solubility in nitric acid, whilst its power of decolorising perman-



ganate solution and the fact of its glowing like tinder on being heated upon platinum foil seemed to indicate the presence of a compound of the brown lead suboxide with the yellow oxide, the two colours together producing red in a similar manner as in the analogous compound of the brown lead dioxide with the yellow lead oxide. The commercial samples of coloured lead carbonate showed the red coloration through their whole mass. The carbonate being very predominant, it was impossible to detect the lead suboxide, the presence of which could only, with some probability, be inferred from the slight decolorising action which the samples, even after thorough exhaustion with water, exercised upon permanganate solution.

R. S.

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**On the Change in a Bronze which had been Buried for a long time.** By PRIWOZNIK (Ann. Chem. Pharm., clxiii, 371—376).

THE pieces examined, which were of an indigo-blue colour, were found in the ancient Celtic graves at Salzberg and consisted apparently of portions of a bronze axe. Several layers could be removed from these fragments; the outer one, which was the thickest, was brittle and had a metallic lustre and a density of 4.675. By analysis it was found to consist of cupric sulphide,  $\text{CuS}$ . The compound is therefore covellin or indigo-copper, with which it agrees in all its properties. The second layer was of a greyish black colour and consisted of copper-glance,  $\text{Cu}_2\text{S}$ , mixed with 15 per cent. of tin, which did not occur in the outer layer. The third or inner layer was a black powder and consisted of cuprous sulphide mixed with a considerable amount of tin. The author believes the crust to have been produced by a direct chemical change of the bronze under the influence of soluble sulphides or sulphuretted hydrogen arising from the decomposition of organic matter containing sulphur. In fact, alloys of copper similar to ancient bronze, become coated with an indigo-blue sulphide of copper when exposed for a length of time to the action of yellow ammonium sulphide.

C. E. G.

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## Mineralogical Chemistry.

**Examination of some Masses of Native Iron discovered by Nordenskiöld in Greenland.** By A. DAUBRÉE (Compt. rend., lxxiv, 1543—1550).

IN 1870 Nordenskiöld discovered at Ovivak, in Greenland, fifteen huge masses of native iron, of which one block, calculated to weigh at least 20,000 kilograms, is supposed to be the largest specimen of native iron on record. The whole were found within an area of 50 square meters. A basaltic rock, in close proximity to the masses, contained many fragments of metallic iron, and the detached blocks were also partially encrusted with a rock of similar character; there would ap-

pear to be no doubt but that the iron in the two situations was of identical origin.

Nordenskiöld submitted portions of the iron to analysis, and found it to contain both nickel and cobalt; from this circumstance he concluded that it was of extra-terrestrial origin. Wöhler, who also examined it, was of the same opinion. It must be admitted, however, that the intimate association of the iron with large eruptive masses in the neighbourhood tends to throw considerable doubt upon the accuracy of these conclusions. Several large specimens of iron from both sources were presented to the author, one of which he has carefully examined.

This specimen was of a deep grey colour, almost black, resembling magnetite or graphitic cast-iron. It had a distinct cleavage, but the faces were not regular, and no distinct crystalline system could be seen. It was not ductile, but broke under the hammer, giving a dark brown-red powder, which was strongly attracted by the magnet. On a polished surface a want of uniformity in structure was observable, the brilliant white crystals of schreibersite and brass-yellow crystals of troilite being distinctly visible. At other places the presence of silicates produced deep green lithoïdal patches upon the surface. When treated with cold water the powder yielded a small percentage of sulphate and chloride of calcium with a trace of ferric chloride; in this respect the present specimen differs from an ordinary meteorite, in which the occurrence of calcium chloride has not been previously observed.

The following are the results of a complete analysis—

Iron, metallic .....	40·94
Iron, combined with O, S, and P. ....	30·15
Carbon, combined .....	3·00
Carbon, free .....	1·64
Nickel .....	2·65
Cobalt .....	0·91
Oxygen .....	12·10
As, S, P, Si, Cu, H <sub>2</sub> O, &c. ....	8·61
	<hr/>
	100·00

At the author's request Berthelot examined the same sample. He found that on ignition it gave off a certain quantity of carbon monoxide and dioxide, but that no gaseous hydrocarbons were evolved. He also carefully examined it for graphite, but found none.

These masses of iron from Ovifak are remarkable, not only from their large dimensions, but also from their chemical constitution, in which latter point, as well as in other physical characters, they are totally distinct from the general type of meteorites as at present known. The sharpness of the crystals of the silicates contrasts strongly with the confused crystallisation common in meteorites, to such an extent indeed that it is even possible to detect the cleavage and crystalline form characteristic of certain feldspars, and by the aid of the microscope and polarized light to recognize an arrangement of the crystals such as is seen in labradorite and some varieties of dolerite. Again, the large quantity of soluble salts and calcium sulphate is another distinctive

character, as is also the fact that, although in meteorites, the iron is frequently combined with sulphur, phosphorus, &c., it is rarely if ever combined directly with oxygen, which latter is, in the present instance, the principal form of combination of the iron. This circumstance, as well as the presence of carbon, both free and combined, allies these specimens to the minerals known as carbonaceous meteorites.

On the other hand, they differ still more widely from terrestrial species, such as dolerites and basalts, more especially since they contain nickel, cobalt, and ferrous sulphide.

The author is inclined to think that these masses of iron are not of meteoric origin, but that they have been formed from basaltic rock, and erupted from exceptionally great depths. These basaltic rocks frequently contain as much as 20 per cent. of ferric oxide, and it is not impossible that during their passage to the surface, this oxide may have been partially reduced to the metallic state; at all events, such a supposition would account for most of the phenomena observed. This reduction would be especially probable in Greenland, where large deposits of lignite occur, and the presence of carbon in the masses might perhaps be accounted for in a similar manner. Against this must be set the fact that these specimens contain matter which decomposes or volatilises at a very moderate heat, which would be incompatible with their passing through such a highly heated region, as the presence of crystallised and anhydrous silicates would seem to imply.

It has been noticed by Stammer and others that carbonic oxide, in presence of iron or iron oxide, produces, under certain circumstances, a deposit of carbon, of which a certain portion combines directly with the iron.

This reaction the author has endeavoured to utilise as a synthetical method, not so much with the intention of preparing artificial meteorites, as to be enabled, by studying the phenomena which occur, to explain perhaps more satisfactorily the circumstances which attend the natural formation of masses of native iron, such as he has described in detail in the present paper.

J. W.

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**Condition of Vesuvius, and Composition of Gases Evolved in the Campi Flegrei, June, 1869.** By M. GORCEIX (Compt. rend., lxxv, 154—156).

AFTER alluding briefly to the physical appearance of Vesuvius as seen in 1869, the author details the results of his analyses of the gases evolved in the district known as the "Campi Flegrei." These gases were carefully examined by Deville in 1862, and by Fouqué in 1865; the author has followed in the steps of those chemists, and has, whenever it was possible, collected the gases at nearly the same points.

A small constant variation was observed in gas issuing from one and the same orifice, to such an extent that two consecutive analyses scarcely ever gave identical results; it was not probable, therefore, that any uniformity would be traceable in the gas from different centres of emanation, or that the present results would correspond closely with those of previous experimenters.



As a rule the gas evolved consisted mainly of carbonic anhydride, mixed with about 5 per cent. of sulphuretted hydrogen, less than 1 per cent. of oxygen, and from 5 to 10 per cent. of nitrogen; the percentage of the latter gas, however, varied greatly, sometimes increasing to the extent of 50 or 60 per cent., with a proportional decrease in the amount of carbonic anhydride. In some instances small quantities of marsh gas were detected.

At Lake Agnano, at the *Grotta del Cane*, the gas which escaped was pure carbonic anhydride; in the *Grotta d'Ammoniaca* the sulphuretted hydrogen present in 1862 was no longer capable of being detected. At the *Grotta di Solfo* the marsh-gas was mixed with a small quantity of hydrogen, but olefiant gas was absent, while the sulphuretted hydrogen which had disappeared in 1865 was again present in notable proportions. At Castellammare this same gas had reappeared, and the proportion of carbonic anhydride had considerably augmented.

J. W.

**Absence of Combustible Gas in the Emanations of the Caldeira de Furnas, San Miguel, Azores.** By CH. SAINTE-CLAIRE DEVILLE (Compt. rend., lxxv, 115).

IN 1867 M. Janssen and the author examined the gases evolved by the Grande Caldeira of Furnas, and found them to consist wholly of carbonic anhydride, sulphuretted hydrogen, and a trace of nitrogen, hydrogen and other combustible gases being absent. The recent experiments of M. Fouqué, communicated by letter to the author, corroborate the above results. The residue left after treating 2,500 c.c. of the gas with potash was less than 1 c.c., and was incombustible.

It would seem, therefore, that the gaseous emanations of the Caldeiras differ materially in composition from those of the Geysers of Iceland, and from the Soffioni of Tuscany, since the latter invariably contain both hydrogen and carburetted hydrogen. They more closely resemble the Solfataras of certain active volcanic districts.

J. W.

**Gases Evolved from the Volcanic Island of Santorin (Grecian Archipelago) after the Eruption of 1866.** By M. GORCEIX (Compt. rend., lxxv, 270—272).

BESIDES carbon dioxide, oxygen and nitrogen, the proportions of which varied from day to day, and even from hour to hour (vide N in table), traces of hydrogen, hydrosulphuric acid, and marsh-gas were detected. In April, 1870, acid vapours (temp. about 115°) were still issuing at two points, the gas evolved having the following composition:—

Gas evolved April 12, 1870.	Fumarole M.	Fumarole N.	
		Sample 1.	Sample 2.
Hydrochloric acid .....	19·4	1·0	} 28·4
Sulphurous acid .....	12·0	0·4	
Carbon dioxide .....	68·5	98·5	
Oxygen .....	none	none	14·0
Nitrogen .....	none	none	57·3
	99·9	99·9	99·7

An analysis of the gas contained in the sea water on the coast (date not stated) gave:—

Carbon dioxide.....	25·5
Oxygen.....	10·1
Nitrogen .....	64·3
	99·9

B. J. G.

## Organic Chemistry.

**Hydrocarbons from Pechelbronn Petroleum, continued** (see this Journal [2] ix, 1025). By J. LE BEL (Compt. rend., lxxv, 267—269).

BESIDES the amylene hydriodide, boiling at 145°, the action of hydriodic acid on the hydrocarbon distilling at 30°—40°, produces a hydriodide boiling at 130°. These compounds are easily separated, since the latter alone is formed in the cold, whereas the former requires hot acid. On account, however, of the violence of the reaction, and the instability of the above compounds, it is better to replace the hydriodic by hydrochloric acid.

Applied to the hydrocarbons distilling at 60°—70°, this method yields two hexylene hydrochlorides, one boiling at 111°—113°, the other at 121°—122°. The hexylene can be transformed into the iso-alcohol, as in the case of the amylene and butylene, with sulphuric acid. The conjugated sulpho-compound first formed is believed to be analogous to ethylsulphuric acid, although it does not form salts, being decomposed, even by water, into dihexylene and isohexyl alcohol.

B. J. G.

**Researches on the Fermentation Alcohols.** By I. PIERRE and E. PUCHOT (Ann. Chem. Pharm., clxiii, 253—295).

THIS paper contains a *résumé* of the author's examination of the volatile products obtained on fermentation of sugar beet, of various kinds of grain, and of molasses.

The separation of the products was effected by fractional distillation in an apparatus the same in principle as that employed by Warren to separate the hydrocarbons in petroleum oil. The preliminary rectifications, however, were executed in the distillery from which the authors obtained the raw material for their researches.

The first runnings were found to contain, besides ethyl alcohol, at least 3 volume per cent. of aldehyde and some acetic ether. The after runnings contained ethyl alcohol, about 3 to 4 per cent. of (iso) butyl alcohol,  $2\frac{1}{2}$  to 3 per cent. of (normal) propyl alcohol, and at least 50 per cent. of amyl alcohol. The presence of other substances was also often noticed, but these could not be isolated in a state of purity.

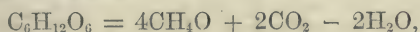
The fusel-oil obtained on rectification of cider contained as much as 6 to 8 per cent. of propyl alcohol, besides ethyl alcohol, but no appreciable amount either of butyl or of amyl alcohol.

The separation of the above-mentioned alcohols by distillation could only be effected after the crude product had been rendered completely anhydrous. Some idea of the enormous quantity of crude material operated upon by the authors will be obtained when it is stated that no less than 30 litres of pure propyl alcohol were isolated during the research.

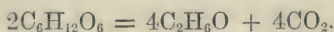
The formation of a variety of alcohols from sugar by fermentation may be expressed by the general equation—



The formation of methyl alcohol ( $n = 1$ ), the possibility of which is represented by the equation



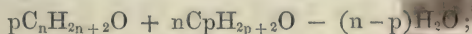
must thus be accompanied by the assimilation of water, whereas that of ethyl alcohol ( $n = 2$ ) takes place without either separation or assimilation of water, thus:—



In all other cases water is eliminated, as, for example, in the formation of propyl alcohol ( $n = 3$ ):—



It may also even be assumed that the different alcohols are convertible into each other, according to the general formula—



the lower members into the higher by the elimination of water, the higher members into the lower by assimilation of water. The authors propose, therefore, having regard to the possibility of the formation of propyl, butyl, or amyl alcohol, in the manner expressed by this equation, to examine the residues obtained in the manufacture of ether, and indeed to study the action of sulphuric acid of different degrees of concentration on ethyl alcohol.

*Propyl Alcohol.*—The preparation and physical properties—boiling



point, specific gravity at different temperatures, &c.,—of this alcohol, and of the following derivatives: propyl aldehyde, chloride, bromide, iodide, formate, acetate, propionate, butyrate, and valerate, are described (this *Journal*, ix, 523, 808, 903).

*Butyl Alcohol*.—The derivatives of this alcohol which are described are: the aldehyde, the chloride, bromide iodide, formate, acetate, propionate, butyrate, and valerate (this *Journal*, ix, 524, 809).

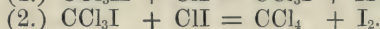
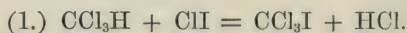
*Amyl Alcohol*.—The boiling point of this alcohol under normal pressure, according to the authors, is  $130^{\circ}$ — $130\cdot2^{\circ}$ ,\* and not  $131\cdot8^{\circ}$ — $132^{\circ}$ , as usually stated. A column, 20 cm. long, of the alcohol produced a rotation of  $8\cdot5$  scale divisions to the left in a Soleil-Dubosq apparatus. Amyl aldehyde, butyrate, and valerate (this *Journal*, ix, 1020) are described; also the preparation and properties of methyl and ethyl valerate, and of ethyl propionate.

In conclusion the authors discuss their observations on the simultaneous distillation of water and certain alcohols insoluble therein (this *Journal*, ix, 1029).

H. E. A.

**Action of Iodine Protochloride and of Bromine on Chloroform.** By C. FRIEDEL and R. D. SILVA (Bull. Soc. Chim. de Paris [2], xvii, 537—539).

In the hope of obtaining carbon trichloriodide,  $\text{CCl}_3\text{I}$ , dry iodine protochloride and chloroform were heated together in a sealed tube at  $160^{\circ}$ — $170^{\circ}$ . Hydrochloric acid was evolved, and allowed to escape from time to time by opening the tube, much iodine being liberated. Carbon tetrachloride formed the main bulk of the product, but it contained a small quantity of an iodated compound boiling at a higher point, it being probable that carbon trichloriodide is first formed, and then acted on by iodine protochloride, thus:—



A similar reaction probably takes place when iodine protochloride acts on the iodides of alcohol-radicals, since these are found to be transformed by it into chlorides. This also explains the statement made by the authors (p. 889), that the same reagent converts propylene into propylene chloride; much iodine is liberated in that case also, and the chloride formed contains a small quantity of an iodine compound boiling at a higher temperature, which is probably propylene chloriodide.

When chloroform is treated with bromine in the same way as above described in the case of iodine protochloride, it is converted into trichlorobromoform,  $\text{CCl}_3\text{Br}$  (see also *Bull. Soc. Chim.* [2], xvii, 212), a liquid boiling at  $103^{\circ}$ — $104^{\circ}$  at 752 mm., density 2.063 at  $0^{\circ}$ , 2.016 at  $25^{\circ}$ . When it is mixed with ether and acted on by sodium, its chlorine and bromine are both slowly attacked. When it is heated alone with

\* No allusion is made to the fact that this fermentation alcohol is a mixture of two isomerides.

sodium, no reaction occurs, but with potassium a violent explosion takes place. B. J. G.

**On Chloropicrin.** By A. COSSA (*Gazzetta Chimica Italiana*, ii, 181—184).

In preparing chloropicrin by Stenhouse's method (*Phil. Mag.*, xxxiii, 53), the calcium hypochlorite should be quite fresh and dry. After mixing with the picric acid, the whole should be passed through a sieve, to retain any lumps, which often cause explosion. The best temperature for the reaction is 45° C. The chloropicrin thus obtained boils at 112·8°, at 743 mm. pressure, and, although the contrary has been stated, it is found to distil without decomposition. When it is suddenly heated to a temperature above its boiling-point, and the vapour passed through a red-hot tube, it decomposes without explosion, as is also the case when sodium or potassium is fused in it. Chloropicrin readily dissolves iodine, the colour of the solution being deeper than that of iodine in chloroform. It also dissolves cinnamic and benzoic acid, resins, and most substances rich in carbon, including that modification of dinitro-naphthalene which is so difficultly soluble in alcohol. It is miscible in all proportions with benzene, amyl alcohol, carbon disulphide, and absolute alcohol. At 11° C. 1 vol. of 80·5 per cent. alcohol dissolves 3·7 vols., and 1 vol. 78 per cent. alcohol 1·3 vols. chloropicrin; 1 vol. ether dissolves only 0·3 vol.

The author transformed chloroform directly into chloropicrin, following Mills' process (*Chem. Soc. Journ.*, ix, 641), but with addition of oil of vitriol.

The reaction which takes place when ammonium sulphide is added to chloropicrin, or when hydrosulphuric acid is passed into a solution of chloropicrin in ammoniacal alcohol, is very energetic, and affords the best means of detecting small quantities of chloropicrin in very dilute alcoholic solution. The liquid becomes hot, a deep red colour is produced, sulphur is set free, and much ammonium chloride formed.

Chloropicrin has a more violent action on the respiratory mucous membrane than either chlorine or nitrous fumes, causing suffocation and spitting of blood.

B. J. G.

**Preparation of Propylene Chloride and Propylene Chlorobromide.** By C. FRIEDEL and R. D. SILVA (*Bull. Soc. Chim. de Paris* [2], xvii, 532—537).

PROPYLENE chloride may be obtained by heating in a closed vessel at 170° propylene bromide and mercuric chloride, but the product is so mixed with impurity, that it is better to use the propylene chloriodide described by Maxwell Simpson (*Bull. Soc. Chim.* [1], v, 500), instead of the bromide. The latter compound, heated to 100° with mercuric chloride, readily furnishes propylene chloride, which may also be obtained by employing dry iodine protochloride, instead of its solution, in Simpson's process.

Propylene chlorobromide was unexpectedly obtained, when an attempt

was made to produce propylene chloride by heating together propylene bromide and mercuric chloride, at the boiling point of the bromide, in a "reflex apparatus." It was proved that the chlorobromide was a true compound, and not a mixture presenting the phenomenon of "adhesion" noticed by Baner, Friedel, and Crafts, by distilling weighed quantities of propylene chloride and bromide together, and practically recovering each at its own boiling point. A better proof still is that when the chlorobromide is treated with alcoholic potash, there is no bromopropylene formed, but only chloropropylene. This reaction renders possible the second only of the two formulæ,  $\text{CH}_3\text{CHBr}\cdot\text{CH}_2\text{Cl}$ , and  $\text{CH}_3\text{CHCl}\cdot\text{CH}_2\text{Br}$ , as a proper expression of the constitution of propylene chlorobromide, which is a limpid, colourless liquid, boiling at  $120^\circ$ ; sp. gr. at  $0^\circ = 1.585$ , at  $16^\circ = 1.475$ ; vapour-density, 5.52 (theory, 5.45).

The above process is not adapted for the production of ethylene or amylene chlorobromide.

B. J. G.

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**Action of Potassium Cyanide on Allyl Iodide.** By A. CLAUS (Deut. Chem. Ges. Ber., v, 612).

THE circumstance that dichloroglycide, when treated with alcoholic potassium cyanide, yields a tri-carboxyl acid (tricarballic acid) leads to the question whether this kind of reaction is general in the case of organic chlorides, &c., derived from hydrocarbons containing doubly associated carbon atoms. When two molecules of potassium cyanide and one of pure allyl iodide are heated together in a sealed tube in a salt-bath for two days, no pressure or smell of ammonia is noticeable on opening the tube. After treatment with caustic potash, a mixture of potash-salts is obtained, which, on distillation with sulphuric acid, yields two acids, one volatile with aqueous vapour (crotonic acid), the other non-volatile, solid, crystallisable, and soluble in ether; this latter may also be separated as lead-salt after slight supersaturation of the alkaline liquid with dilute nitric acid; it appears to be a well marked bibasic acid of formula,  $\text{C}_5\text{H}_8\text{O}_4$ , and is probably identical with pyrotartaric acid.

This power of combination with the elements of hydrocyanic acid does not appear to be possessed by the acids derived from non-saturated hydrocarbons; acrylic acid, oleic acid, and crotonic acid when treated with alcoholic potassium cyanide, do not thus yield bibasic acids. The author proposes to examine whether chlorinated, &c., acids of this class are capable of undergoing such a change; thus chlorocrotonic acid should yield a tribasic acid (tricarballic?).

C. R. A. W.

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**Vinyl Compounds.** By E. BAUMANN (Ann. Chem. Pharm., clxiii, 308—322).

SODIUM methylate acts on vinyl iodide or bromide at the ordinary temperature, even when shaded from sunlight; the products are the same as when the action takes place at a higher temperature, being acetylene, sodium bromide, methyl alcohol, and a trace of a substance which may



be allyl alcohol, as it gives rise to an odour exactly resembling that of acrolein when treated with dilute sulphuric acid and potassium dichromate.

Pure potassium cyanide (prepared by saturating alcoholic potash with gaseous hydrocyanic acid) and silver cyanide, have practically no action on vinyl bromide, even after several hours' heating at 140°—150°.

When vinyl bromide is kept in a sealed tube in the dark, no change ensues, even after several weeks; but if exposed to direct sunlight, it becomes changed into an isomeric, solid, non-crystalline, porcelain-like, elastic substance; this change takes place more rapidly with moist bromide than with the perfectly dry substance; the presence of a small quantity of alcohol neither accelerates nor retards the change. This solid substance has the sp. gr. 2.075, whereas the liquid bromide has the sp. gr. 1.52 (Regnault). It begins to decompose at 125°—130°, and is but little acted on by boiling alcoholic potash; twelve hours heating to 180°—200°, with this reagent, however, forms a brown-black substance, insoluble in all menstrua, all bromine being removed from it without any evolution of gas. Sulphuric acid carbonises the substance on being heated with it; boiling nitric acid has but little action on it; bromine dissolves it, forming a loose compound, which splits up into bromine, and the original substance on treatment with water, alcohol, or alkalis.

Vinyl chloride undergoes a change by the action of sunlight, producing an isomeride of similar appearance and properties to the above described substance. The sp. gr. of the solid modification is 1.406; it can be heated to 130° without decomposition, but melts to a black brown mass at a higher temperature; it is not dissolved by bromine.

Dichlorinated ethylene (chlorinated vinyl chloride) boiling at 36°, also becomes changed into a solid isomeride by the action of light. This body has been described by Regnault, and a similar modification of brominated vinyl bromide by Sawitsch.

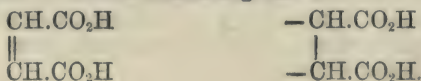
The preparation of vinyl iodide from ethylene iodide is difficult, the yield being very small; it is not obtainable by the action of potassium iodide on vinyl bromide; sunlight decomposes it, setting free iodine, which probably prevents the isomeric transformation of the unaltered iodide, as a trace of free iodine prevents this change in the case of vinyl bromide.

C. R. A. W.

### On the Molecular Weights of Fumaric Acid and Maleic Acid.

By H. HUEBNER and G. SCHREIBER (*Zeitschr. f. Chem.* [2], vii, 712—715).

To explain the isomerism of these two acids, both of which are converted into succinic acid by addition of hydrogen, it must be assumed either that they are polymerides, or that one of them contains carbon-atoms with free combining units, thus—



To decide this question, the authors have determined the vapour-densities of ethyl fumarate and of maleic anhydride, which two compounds can be readily obtained pure, and volatilise without decomposition. The result was that the two acids have the same molecular weight.

C. S.

**Notice on Ketones.** By E. SCHMIDT (Deut. Chem. Ges. Ber., v, 597).

THE ketones examined were prepared by heating in a wide iron tube placed on a combustion furnace the lime salts of the corresponding acids mixed with calcium carbonate to prevent fluxing: if lime be taken instead, as usually recommended, a larger quantity of aldehydes, &c., is produced. The heating was gradually carried on from the back to the front of the tube; a much greater yield was obtained by this mode of operation than by the ordinary plan of using a retort, the formation of bye-products being in great part avoided: the crude products were dehydrated by calcium chloride and repeatedly fractionally distilled. By this means *propione*, *butyrone*, *valerone*, *caprone* and *methyl-caprone* were obtained, exhibiting the following boiling points and specific gravities:—

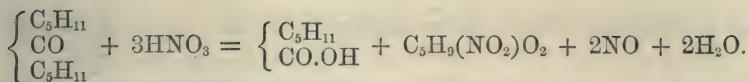
	Boiling point.	Specific gravity.
Propione .....	100°—101°	0·813 at 20° (0·815 at 17·5° Popoff)
Butyrone .....	144°	0·819 at 20° (0·820 at 20° Kurz)
Valerone .....	181°—182°	0·833 at 20°
Caprone .....	220°—221°	0·822 at 20°
Methyl-caprone....	155°—166°	0·813 at 20° (0·828 at 0° Popoff).

The boiling points of the last three differ from those formed by other experimenters: Löwig found that valerone boiled under 100°; Chancel concluded that Löwig had examined the aldehyde and not the ketone; Ebersbach found 164°—166°. Similarly Brazier and Gosleth found that caprone boiled at 165°; and Popoff gives 144° as the boiling point of methyl-caprone, while 152° is given in Schorlemmer's "Lehrbuch."

Popoff describes propione as giving crystals with sodium bisulphite; the author could not find any crystalline compound formed in this manner by any of the ketones examined, save methyl-caprone; apparently only those mixed ketones which contain the methyl group, and dimethyl ketone (acetone), are capable of forming these crystalline compounds.

By the action of nitric acid, butyrone yields nitropropionic acid, as already found by Chancel and by Kurz; the potassium salt has the formula,  $C_3H_4(NO_2)KO_2 + H_2O$ .

Valerone constitutes only about 10 per cent. of the crude distillate from calcium valerate, the majority being valeric aldehyde boiling at 97°—98°: nitric acid acts violently on valerone, forming nitrobutyric, valerianic, and oxalic acids. Similarly caprone gives rise to caproic acid and nitrovalerianic acid:



Methyl-caprone when thus treated yields no nitro-acid, but only caproic and acetic acids: oxalic acid is produced in some quantity in all these cases. Sodium bisulphite gives a copious supply of crystals with methyl caprone.

C. R. A. W.

**Preparation of Orthoxylene from Liquid Bromotoluene.** By P. JANNASCH and H. HUEBNER (*Zeitschr. f. Chem.* [2], vii, 706—709).

LIQUID bromotoluene, freed as much as possible from the solid compound by means of a freezing mixture, and distilling at  $179^\circ$ — $180^\circ$ , was diluted with pure benzene, ethyl iodide and sodium were added, and the mixture kept cold. The dimethylbenzene thus produced boiled at  $141^\circ$ — $143^\circ$ , and yielded by oxidation with dilute nitric acid, *paratoluic acid* and *orthotoluic acid* in the proportion of one to a little more than two. As the latter acid is much more soluble than the former, it may be assumed that the hydrocarbon contained at least 75 per cent. of orthoxylene. This is another example showing how difficult it is to separate completely a liquid compound from a solid which is dissolved in it, if both have nearly the same boiling point.

C. S.

**Reduction of Isoxylene and Aromatic Hydrocarbons in general.** By FELIX WREDEN (*Deut. Chem. Ges. Ber.*, v, 608).

In order to obtain reduction-products from isoxylene, 2 c.c.'s of the hydrocarbon and 12 of hydrodic acid saturated at  $0^\circ$  were heated with  $\frac{1}{2}$  gram. of red phosphorus to  $230^\circ$ — $240^\circ$ ; phosphonium iodide was formed at first, and finally this disappeared, iodine being set free; on opening the tube hydriodic acid gas and free hydrogen escaped. With the above proportions, there is no fear of tubes bursting, but with larger quantities or greater proportions of phosphorus, no tube (out of five) was found to withstand the pressure. The oily product of 24 hours' action (12 at  $170^\circ$ , 12 at  $240^\circ$ ) was digested with bromine; a bromide distilling at  $124^\circ$ — $140^\circ$  was obtained; this was heated to  $100^\circ$  for six hours with strong sulphuric acid in a sealed tube, then digested with sodium at  $100^\circ$  for 8 hours. The product appeared to contain a little oxygen, but after three hours' digestion with sodium at  $150^\circ$ , it gave numbers agreeing with a mixture of  $\text{C}_8\text{H}_{16}$  and  $\text{C}_8\text{H}_{18}$ ; its vapour density also agreed with this supposition, while its boiling point ( $115^\circ$ — $118^\circ$ ), its specific gravity (0.76 to 0.77), its power of absorbing oxygen, and its smell agreed closely with the hydrocarbons of analogous composition derived from camphoric acid.

C. R. A. W.



**On the Nature of Some Bromosalicylic Acids.** By H. HUEBNER and C. HEINZERLING (Zeitschr. f. Chem. [2], vii, 709—711).

BROMOBENZOIC acid yields two isomeric nitro-compounds. By converting them into amidated acids and acting on their solution in dilute hydrochloric acid with potassium nitrite, they are converted into the corresponding bromoxybenzoic acids.

$\alpha$ -Bromoxybenzoic acid is not easily obtained, as it is readily decomposed during its formation. It is very soluble, and crystallises in small needles, melting at  $219^{\circ}$ — $220^{\circ}$ . Its aqueous solution is coloured dark reddish-blue by ferric chloride.  $(C_6H_3Br(OH)CO_2)_2Pb$  is a white precipitate produced by adding lead acetate to a solution of the ammonium salt.

$\beta$ -Bromoxybenzoic acid is more readily formed. It crystallises in long needles, melting at  $164^{\circ}$ — $165^{\circ}$ ; the aqueous solution gives a reddish-blue colour with ferric chloride. The alkali-salts are very soluble in water.  $(C_6H_3Br(OH)CO_2)_2Ba$  forms colourless needles, containing water of crystallisation.

$(C_6H_3Br(OH)CO_2)_2Pb$  is a white precipitate, sparingly soluble in cold and hot water.  $C_6H_3BrO(CO_2)Pb$  separates in needles on evaporating a dilute solution of the barium salt with lead acetate.  $C_6H_3(OH)CO_2Ag$  is a white insoluble precipitate.  $(C_6H_3(OH)CO_2)_2Cu$  is obtained as a yellowish-green precipitate by adding copper acetate to a solution of the ammonium or barium salt; from a dilute solution it crystallises in plates.

$\beta$ -Bromoxybenzoic acid is no doubt identical with the bromosalicylic acid which Henry prepared by the action of phosphorous bromide on salicylic acid. The same acid appears to be produced by adding salicylic acid to a solution of bromine in carbon disulphide; it crystallises in long thick needles, melting at  $164^{\circ}$ — $165^{\circ}$ . The barium salt,  $(C_6H_3Br(OH)CO_2)_2Ba + 3H_2O$ , is readily soluble, and forms shining needles. The lead salt is a white and the copper salt a greenish-yellow precipitate.

C. S.

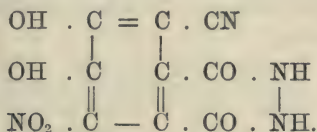
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**A New Derivative of Styphnic Acid.** By J. SCHREDER (Ann. Chem. Pharm., clxiii, 297—307).

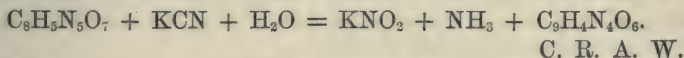
WHEN styphnic acid (trinitroresorcin) is acted on by two proportions of potassium cyanide, a dark red-brown liquid is obtained from which a brown non-crystalline mud separates; but if the neutral potassium salt be employed instead of the free acid, a crystalline difficultly soluble potassium salt is obtained, which, when treated with sulphuric acid, yields a crystalline compound named by the author *resorcin-indophan*. This substance is easily soluble in cold water with a pure blue violet colour, insoluble in alcohol and ether; strong hot acetic acid takes up a little, and cold concentrated sulphuric acid dissolves it without decomposition; its formula is  $C_9H_4N_4O_6 \cdot 2 \text{ at. } H_2$ , being replaceable by metals; the potassium, sodium, and barium-compounds have been analysed. Nitric acid oxidises resorcin-indophan to a yellow syrup containing oxalic acid; chlorine water bleaches its solution,

producing apparently chloropicrin; sodium-amalgam produces the insoluble sodium compound which is unacted on by nascent hydrogen; acetyl chloride has no action.

Heating with soda-lime eliminates three-fourths of the nitrogen as ammonia. Hence not more than one  $\text{NO}_2$  group can be contained in the compound; the author ascribes to resorcin-indophan, the formula—



viewing it as derived from (hypothetical) oxyiso-purpuric acid by the reaction:—



**Camphoric Acid.** By F. WREDEN (Ann. Chem. Pharm., clxiii, 323—342, from the Journal of the Russian Chemical Society).

A MUCH larger yield of acid than heretofore obtained can be procured by dissolving 150 grams of camphor in two litres of nitric acid of 1.27 sp. gr. (1 vol. water to 2 vols. concentrated acid), and heating for 50 hours in a water-bath in a large flask with a long tube cemented to the mouth. This acts as a condenser, the upper end being bent to a right angle and leading into the chimney. Thus treated, camphor yields more than half its weight of purified acid.

The reactions of camphoric acid show that it is a bibasic acid, and that its formula is to be written  $\text{C}_8\text{H}_{14}(\text{CO.OH})_2$ . Four modifications have hitherto been described, viz., dextro-rotatory, lævo-rotatory, inactive, produced by mixing the first two (para-camphoric), and the inactive insoluble variety, produced by decomposing para-camphoric ether with caustic potash. A fifth is obtainable by heating for 30 hours to  $150^\circ$ — $160^\circ$ , camphoric acid with hydriodic acid of sp. gr. 1.6 (5 grams to 30 c.c.), or with fuming hydrochloric acid saturated at  $0^\circ$ . Its crystals contain no water, and are more soluble in water than the ordinary variety. It melts at  $113^\circ$ , and is much less readily converted into anhydride. The author terms this variety *mesocamphoric acid*, as it is inactive, and bears to camphoric acid a relation similar to that of mesotartaric to racemic acid.

Under different conditions the action of hydriodic acid on camphoric acid is to produce hydrocarbons,  $\text{C}_8\text{H}_{14}$ ,  $\text{C}_8\text{H}_{16}$ ,  $\text{C}_8\text{H}_{18}$ : the first two of these have been described as  $\text{C}_9\text{H}_{16}$  (campholene) and  $\text{C}_9\text{H}_{18}$  by Gille, Keyl, and others. The formation of the lowest is expressed by the reaction  $\text{C}_{10}\text{H}_{16}\text{O}_4 = \text{H}_2\text{O} + \text{CO} + \text{CO}_2 + \text{C}_8\text{H}_{14}$ .

By the action of bromine on camphoric anhydride or acid there is formed ultimately *bromocamphoric anhydride*,  $\text{C}_{10}\text{H}_{18}\text{BrO}_3$ , water being eliminated in the second case. This is soluble in alcohol and chloroform, being partly decomposed by boiling alcohol of 95 per cent. On

boiling with water, this compound yields *oxycamphoric anhydride* (camphanic acid), recently obtained by Kachler from camphoric acid. This acid has the formula  $C_{10}H_{14}O_4$ , and acts as a bibasic acid, its salts containing water of crystallisation lost at  $100^\circ$ . It yields a mono-ethylic ether by the action of hydrogen chloride on an alcoholic solution, the same substance being produced by the action of alcohol on the brominated anhydride. The calcium salt when distilled furnishes a hydrocarbon,  $C_8H_{14}$ , resembling the terpenes, of sp. gr. 0.814 at  $0^\circ$ , boiling at  $119^\circ$ , and capable of absorbing oxygen. The same substance is obtained by heating the oxyanhydride with water to  $180^\circ$  in sealed tubes. This is probably identical with the lowest hydrocarbon obtained by the action of hydriodic acid on camphoric acid.

By heating bromocamphoric anhydride with ammonia, *amidocamphoric anhydride*,  $C_{10}H_{13}(NH_2)O_3$  is formed. Nitrous acid converts this into the oxyanhydride. On heating with 10 per cent. alkaline solutions it yields *amidocamphoric acid*,  $C_{10}H_{15}(NH_2)O_4 \cdot H_2O$ , the water of crystallisation being lost at  $85^\circ$ .

The above described substances are all solid, having the following melting points:—

Camphoric anhydride, $C_{10}H_{14}O_3$ .....	$217^\circ$
Bromocamphoric anhydride, $C_{10}H_{13}BrO_3$ .....	$215^\circ$
Oxycamphoric anhydride, $C_{10}H_{13}(OH)O_3$ .....	$201^\circ$
Oxethylcamphoric anhydride, $C_{10}H_{13}(OC_2H_5)O_3$ ..	$63^\circ$
Amidocamphoric anhydride, $C_{10}H_{13}(NH_2)O_3$ ....	$208^\circ$
Acid from ditto, $C_{10}H_{15}(NH_2)O_4$ .....	$160^\circ$

The author views oxycamphoric anhydride as the representative of a new class of substances which are at once anhydrides and bibasic acids.

C. R. A. W.

### Azophenylene from Para-azobenzoic Acid (Azodracrylic Acid).

By A. CLAUS (Deut. Chem. Ges. Ber., v, 610).

ROSENACK has shown that azobenzoate of calcium yields azophenylene on distillation. On repeating his experiments with azodracrylic acid the same product was obtained. After crystallisation from hot alcohol the product melted at  $171^\circ$ , and corresponded in all respects with Rosenack's product, which melted at  $170^\circ$ — $171^\circ$ .

C. R. A. W.

### Note on Tyrosine. By L. BARTH (Ann. Chem. Pharm., clxiii, 296).

IN consequence of Beilstein and Kuhlberg's observations on a possible synthesis of tyrosin (this *Journal*, x, 709), the author makes the following statement. He was led by former researches to regard it as an oxyphenylamidopropionic acid of the para series, and therefore to attempt its formation from paracoumaric (paraoxycinnamic) acid by converting this acid by Glaser's reaction into oxyphenyl-chlorolactic acid, and acting on the latter with ammonia. He has in this way obtained, as



end-product, crystals still contaminated with impurities, which, to judge from their qualitative reactions may perhaps be tyrosine.

H. E. A.

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## Physiological Chemistry.

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**Influence of different Earthy Phosphates mixed with the Food on the Composition of the Bones.** By H. WEISKE-PROSKAU (*Zeitschr. f. Biologie*, viii, 239—245).

PAPILLON had found that considerable quantities of earthy phosphates—strontium phosphates among others—mixed with the food, were deposited in the bones. The author, with the assistance of E. Wildt, repeated these experiments on young and old rabbits, but could not find the slightest trace of strontia, or any noteworthy increase of the magnesia, lime, or phosphoric acid in the bones when earthy phosphates were mixed with the food. The age of the animal has an influence on the composition of the bones, those of old rabbits containing more salts than those of young ones. The percentage composition of the bone-ash is much alike in both, but the proportion of magnesia seems to be somewhat higher, and of lime somewhat lower, in young animals. The percentage amount of phosphoric acid is almost the same in all bones, and is on an average 42·17 per cent.

T. L. B.

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**On the Amount of Caffeine contained in Coffee, and on its Physiological Action.** By HERMANN AUBERT (*Pflüger's Archiv. für Physiologie*, v, 589—628).

ALTHOUGH the quantity of caffeine contained in raw coffee is known, no attempt has ever been made to ascertain how much of the alkaloid is contained in a cup of coffee, and it is also uncertain whether the beans should be slightly or strongly roasted, and whether the ground coffee must be boiled to extract its active principles or simple infusion is sufficient. By extracting the coffee with water, either by percolation or decoction, and evaporating to a syrup, which is then treated from five to eight times with chloroform at nearly 60° till all the caffeine has been dissolved out, he obtains a larger quantity than previous experimenters. Raw beans of the yellow Java kind yielded 0·709—0·849 per cent. by this method, while they gave only 0·474 by Garot's method of precipitation with basic lead acetate. When much roasted, coffee loses a certain quantity of caffeine, which sublimes, whereas it loses none by slight roasting. Notwithstanding this, the coffee made in the usual way by percolation from strongly roasted coffee contains rather more caffeine than that made from an equal weight of slightly roasted coffee, as the roasting renders it more easy to extract.

When coffee is prepared in the usual domestic fashion by pouring six to ten times its weight of boiling water three or four times over ground coffee, nearly the whole of the caffeine is extracted, hardly one-

fifth of it remaining in the grounds. The quantity of caffeine in a cup of coffee prepared from  $16\frac{2}{3}$  grams of coffee is about 0.1 to 0.12 gram. A cup of tea prepared in the ordinary way from 5—6 grams of Pekoe tea contains also about 0.1 to 0.12 grams of caffeine. Caffeine acts upon the spinal cord and causes tetanus in doses of 0.005 gram for a frog, injected subcutaneously; for a rabbit, 0.120 gram (injected into the jugular vein), for cats; 0.200, injected in the same way; and the same quantity for dogs. It has a peculiar action on the muscles of frogs, especially when directly applied to them, causing them to become rigid and white, apparently from coagulation of the myosin. It does not exert this action on the muscles of mammalia. The tetanus is removed by artificial respiration, and if this process is kept up for about a quarter of an hour no recurrence of the tetanus takes place, even though the respiration is then discontinued, showing that the caffeine is quickly eliminated or destroyed in the organism. Occasionally it produces a paralysis of the hind legs in rabbits, but the author is uncertain to what cause this is to be attributed. It quickens the heart and at the same time reduces the blood pressure. This effect he believes to be due to stimulation of the cardiac ganglia, combined with diminution of what he regards as cardiac *tone*, due to paralysis of the nerves passing from these ganglia to the muscular substance.

The action of caffeine does not explain the stimulating and reviving action of coffee.

T. L. B.

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**Composition of Goat's Urine on a Purely Vegetable and Purely Animal Diet.** By H. WEISKE-PROSKAU (*Zeitschr. f. Biologie*, viii, 246—250).

Two kids of the same age were taken, and one was quickly weaned and fed on a vegetable diet, while the other was fed exclusively on milk. When both were seven months' old, their urine was collected and compared. That of the first kid, fed on vegetable diet, presented the usual characters of the urine of herbivora, being turbid, alkaline, and effervescing with acids; while that of the second, which was fed on milk, was perfectly clear and strongly acid, like the urine of carnivora. The urine of the first was very concentrated (sp. gr. 1.058), and 100 cub. cent. contained on an average 11.08 grams of solids, 5.19 of ash, and 1.11 of nitrogen. The addition of hydrochloric acid caused a deeply-coloured deposit of hippuric acid to form after some time. When the kid was fed on hay instead of green clover and turnip-leaves, the precipitate of hippuric acid occurred immediately after the addition of the acid, and was much purer and larger, 100 c.c. of urine yielding 1.80 grams of it. The urine of the second animal had a sp. gr. of 1.011, and 100 c.c., and contained, on an average, 1.75 grams of solids, 0.57 of ash, and 0.33 of nitrogen. The addition of hydrochloric acid produced a very slight precipitate after a long time. It contained no uric acid. The urine of the second animal contained a large quantity of phosphates, while the first contained only traces of them, but large quantities of carbonates and sulphates.

T. L. B.

**Researches on Iron in the Blood of an Invertebrate Animal.**

By M. BOUSINGAULT (Compt. rend., lxxv, 173).

THE blood of *Limax flava* is almost colourless, and contains numerous elliptical corpuscles, about the size of the blood-corpuscles in the cow. It has an alkaline reaction, and consists of water 96·095 per cent., dry residue 3·905, ash 0·767, and iron, reckoned in the metallic state, 0·00069 per cent. If iron really formed a constituent of the blood of the limax, it might be expected that, as in the higher animals, it would be present in larger proportion in the blood than in the muscles. At first sight it would appear not to be so, for the limax, freed from its intestines, contained water 84·88, dry residue 15·12, ash 3, and iron 0·001176 per cent., a quantity of iron larger than that in the blood. This is due to the greater proportion of solid residue in the muscles; and when equal quantities of the dry residue of muscle and of blood are compared, the latter is found to contain more than twice as much as the former, the numbers being 0·0177 per cent. of iron in dried blood, and 0·0078 in dried muscle. This proportion is very much smaller than in animals with red blood, the dried blood of the ox containing ten times as much iron as the dried muscle. The actual amount of iron in the blood of the limax is only  $\frac{1}{75}$ th of that in a red blood. The colourless character of the blood is due to the absence of hæmoglobin, or to the presence of an analogous substance in small quantity only, as the blood remains yellowish, and does not acquire a red tint even when concentrated by evaporation.

T. L. B.

**Researches on the Physiological Action of Kinic Acid; Reduction of Ferric Chloride in the Organism.** By M. RABUTEAU (Compt. rend., lxxv, 219—221).

KINIC acid agrees in its action with citric and tartaric acids, and has no active properties peculiar to itself. Its alkaline salts have no taste, and, like those of other organic acids, are converted into carbonates in the body. They cause constipation when injected into the blood, and would probably be purgative if introduced in sufficient quantity into the alimentary canal. Ferric chloride is readily reduced by organic substances. To this reduction is due the blue stain which is produced on the hands after using ferric salts or potassium ferrocyanide. The author considers that ferric salts are reduced to ferrous in the stomach, and are absorbed as such, and that when ferric chloride has been injected into a varicose vein to coagulate the blood, the coagulum which it at first produces afterwards disappears, because the ferric salt is converted into a ferrous salt which hinders the coagulation of the blood instead of inducing it.

T. L. B.

**Is the Compound of Carbonic Oxide with Hæmoglobin a Fixed Compound?** By N. ZUNTZ (Pflüger's Archiv., v, 584—588).

ZUNTZ investigates the relation of carbonic oxide to blood, and puts to stringent proof the dissociation theory of respiration propounded by



Donders (p. 252 of this volume). Donders states, in opposition to generally received opinions, that carbonic oxide may be driven out of blood by oxygen, or hydrogen, or carbonic acid, or even by a temperature of  $0^{\circ}\text{C}$ ., and that it is evacuated from the blood as such without undergoing oxidation into carbonic acid. It is clear, if Donders is right, that it will also be possible to pump the carbonic oxide out of the blood saturated with this gas, even though it may not be quite so easily removed as oxygen.

Both Nawrocki and Pokrowsky deny the possibility of this. Zuntz placed blood saturated with carbonic oxide in the receiver of Pflüger's gas-pump, and found, on warming it to  $37^{\circ}$ — $42^{\circ}$ , that there was an active escape of gas which apparently ceased at the end of half an hour. When the pumping was continued at various intervals, however, fresh quantities of gas were freed. More was again obtained by heating the receiver to  $60^{\circ}$ . The blood so exhausted was found to give the spectrum of reduced hæmoglobin, which was replaced by the spectrum of oxy-hæmoglobin after standing in the air. The hæmoglobin had not undergone decomposition. Two analyses gave exactly the same results. The gas obtained was freed from carbonic acid by caustic potash and from oxygen by potassium pyrogallate. The oxygen obtained, derived in all probability from the air, has no effect in causing a formation of carbonic oxide.

The gas obtained at  $60^{\circ}$  was analysed separately from that at  $40^{\circ}$ . From 31.65 c.c. of dog's blood, sp. gr. 1071, the quantities were—

at  $40^{\circ}\text{C}$ . — 4.607 c.c. CO ( $0^{\circ}$  and 1 m.)

at  $60^{\circ}\text{C}$ . — 0.998 c.c. CO

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Total = 5.605 c.c. CO

*i.e.*, = 17.7 per cent. of the blood-volume.

The chief point to be observed is, that the gas cannot be pumped out all at once, but is evolved at intervals only. Schöffner found that this was also true of carbonic acid, and he attributed it to the progressive development of an acid which set free the gas. Zuntz shows that this supposition is untenable: for he finds by experiment that the same is true of solutions of sodium bicarbonate, which also parts with its carbonic acid in a fitful manner, an effect which cannot in this case be attributed to the development of any acid. These experiments sufficiently account for other investigators not having been able to extract carbonic oxide from the blood, as the process was supposed to be complete when no more gas was evolved after the first pumping. Zuntz also points out some errors in the methods adopted by Pokrowsky. These results must modify received ideas regarding carbonic oxide poisoning. There is no longer need to suppose that carbonic oxide can only be removed from the blood by oxidation into carbonic acid. As long as the heart still beats there is hope, by energetic artificial respiration, of again restoring the blood to its normal condition.

D. F.

**The Glycogenic Function of the Liver and its Relation to Diabetes.** By F. W. DöCK (Pflüger's Archiv., v, 571—583).

THIS is a research from the physiological laboratory of Zurich, giving the results of new experiments on the conditions of glycogen formation in the liver, as well as some very interesting observations on the relations of this to artificial diabetes. In regard to the question from what elements of the food glycogen is formed, though agreeing substantially with Pavy and Tscherinow that it is from the carbohydrates, the author considers that the methods of investigation and analysis adopted by these observers are not free from objection, and he therefore adopts Brücke's method for the qualitative and quantitative determination of glycogen. He found in the first place that after rabbits had been starved for several days, the liver became entirely, or almost entirely, devoid of glycogen, but that if after such a period of starvation injections of sugar were made into the stomach, glycogen appeared in the liver in large amount. If, instead of sugar, injections of albumin or water were made, no glycogen appeared in the liver. No experiments were made with fat, as it has been well established that fat does not cause glycogen formation. The occurrence of glycogen in the liver after injections of sugar into the stomach takes place in a few hours.

He regards it as proved that any excretion of sugar from the organism, as in diabetes, must in the last instance be referred to the carbohydrates of the food, but discusses the question whether diabetes is due to the passage of the sugar directly through the body without previous transformation into glycogen, or whether it is due to increased transformation of glycogen into sugar. That it is not due to diminished combustion of the normal amount of sugar formed by the liver he considers is proved by Pavy's researches, and by the recent experiments of Ludwig and Scheremetjewski, which show that there is no oxidation of sugar when introduced directly into the blood. He induces diabetes in starved rabbits by puncturing the floor of the fourth ventricle, and analyses the liver for glycogen in those which have received injections of sugar into the stomach and in those which have received only water injections.

He finds that after the "sugar puncture" injections of sugar do not cause the appearance of glycogen in the liver, nor does any appreciable quantity of sugar appear in the urine. The injections of sugar into the stomach thus remain unaccounted for. Experiments on diabetes induced by curara afforded a probable explanation of this. It was found that in starved animals under the influence of curara, injections of sugar likewise failed to cause a formation of glycogen in the liver. On the other hand, sugar appeared in the urine in large amount. Apparently therefore it seemed established that diabetes was due to the passage of the sugar of the food directly into the urine without becoming stored up as glycogen in the liver. But on the other hand, it was found that curara caused the occurrence of sugar in the urine even when no injections of sugar had been made, and that too in animals which had been starved long enough to cause the entire disappearance of glycogen from the liver. Hence the theory of diabetes which regards the sugar, simply as that which has passed into the

urine directly from the food is proved insufficient to account for all the phenomena. Dock promises further investigations, but suggests that the explanation is, in all probability, to be sought for in the muscles, which may have the power of storing up glycogen or sugar and retaining it more tenaciously than the liver, capable, under certain conditions, of again being given up and appearing as sugar in the urine.

D. F.

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**The Physiological Action of Trichlorhydrin.** By A. ROMENSKY  
(Pflüger's Archiv., v, 565—570).

ROMENSKY adds a new anæsthetic to the long list of the similar chlorine substitution products of the hydrocarbons of the fatty series. This new substance is trichlorhydrin or trichloropropane,  $C_3H_5Cl_3$ .

One drop of this liquid introduced into the stomach of frogs causes, after a quarter of an hour, weakening of the spontaneous movements and reflex excitability. Ultimately reflex excitability entirely disappears, the heart's action is diminished to twelve beats per minute. This condition lasts four hours. The animal gradually recovers, and next day is quite well.

In rabbits of medium size half a gram, and in larger ones, one gram causes sleep in five minutes, with diminution or entire abnegation of reflex excitability. The respiration is retarded, and the heart is quickened. The sleep lasts from ten minutes to several hours, and complete recovery ensues. In all cases there is first dilatation then contraction of the vessels of the ear. The temperature sinks in all cases, in some as much as three degrees. The blood pressure is first increased and then sinks, and continues to oscillate periodically during the whole period of sleep. Smaller doses cause heaviness and weakness of the voluntary movements.

In dogs, besides the last-mentioned symptoms, vomiting follows the administration of the drug in from  $1\frac{1}{2}$  to  $3\frac{1}{2}$  hours. In man the vomiting, which is invariably caused, forbade the use of large hypnotic doses. Romensky, however, chose to risk the effects on himself, and swallowed two grams in a capsule. After fifteen minutes it caused sleepiness and headache and feeling of heat in the face. This condition lasted two hours without real sleep being induced. The gait was tottering and facial pain was felt. In the night, seven hours after the administration, violent vomiting came on, and catarrh of the stomach remained for two days.

Trichlorhydrin thus acts like the other anæsthetics on the nervous system, but on account of its insolubility and the irritation of the stomach which it induces, it is not well fitted for administration by the mouth. It also produces anæsthesia by inhalation, but on account of its not being very soluble it acts more slowly than chloroform. Trichlorhydrin occupies an intermediate place between chloroform and chloral. Chloroform cannot be given by the stomach and chloral cannot be inhaled, while trichlorhydrin may be applied in either way. It is, however, of no practical value, for it produces gastro-intestinal irritation, and is therefore inferior to chloral, and on account of its small volatility it is not so rapid as chloroform.

D. F.



**Unorganized Ferments.** By G. HÜFNER (J. pr. Chem. [2], v, 372—396).

THE author has adopted von Wittich's method of preparing certain animal ferments, and has investigated their individual action, and the conditions of their activity, with a view to explain the nature of fermentation in general.

In order to obtain the ferment from any organ which contains it, the organ must be freed from blood, finely minced and soaked in absolute alcohol, partly to remove the water and partly to coagulate the soluble albumin; it is then to be freed from alcohol, and soaked for several days in glycerine. The ferment is obtained from the glycerin extract in the form of a powder on the addition of alcohol. These precipitates always contain more or less albumin, which, however, may be removed almost entirely by re-solution in glycerine and reprecipitation by alcohol.

Pancreatic ferment so prepared is a white amorphous powder, containing sulphur and nitrogen, and leaving an ash containing sodium chloride and magnesium phosphate. It acts on starch, fibrin, and fat, like the pancreatic secretion itself. As regards the question whether the substance so prepared is a simple one, or composed of three different elements, each possessed of specific properties, it is concluded, from the remarkable uniformity of the various constituents in four different analyses of as many different specimens, either that one substance predominates, and that the variations which are observed are due to more or less admixture of foreign elements, or that, if there are two or more organic substances in equal, or nearly equal, amount, they do not differ from each other appreciably in their elementary composition.

In order to purify the ferment as much as possible, Hüfner redissolves it in glycerin, and precipitates it by dropping the glycerine extract into a long column of alcohol of 96 per cent. The precipitate is washed with alcohol and ether, and dried over sulphuric acid. It is thus obtained in brittle pieces readily convertible into an extremely light powder. It is quite amorphous, and possesses no trace of organised structure. It still contains ash, sulphur, and nitrogen, and is still active. It is not hygroscopic. Prolonged heating at 100° causes no loss of weight, and no diminution of activity.

Analyses gave the following percentage:—

	I.			II.		
C =	43·25	43·09	—	43·59	—	—
H =	6·80	6·50	—	6·73	—	—
N =	—	—	13·80	—	11·00	—
S =	—	—	—	—	—	0·88
O =	—	—	—	—	—	—
Ash =	—	—	—	—	—	7·04

The ash contained no phosphoric acid or chlorine, and only a trace of magnesia.

The powder is slowly soluble in water. The watery solution re-

sembles solutions of albumin. Both it and the solution in glycerin coagulate on boiling. The solution is precipitated by many agents, which likewise precipitate albumin, and it gives Millon's reaction.

The only marked difference between the precipitated pancreatic ferment and albumin precipitated by alcohol, is that the former is again soluble in distilled water. When coagulation begins, the solution loses its power of digesting fibrin, as well as its diastatic and fat-splitting properties. When coagulation begins (at 70°) fine flocculi separate out, and from the filtrate a second precipitate can be obtained by addition of excess of strong alcohol.

The flocculi have the following percentage composition:—

C, 47.36; H, 7.24; N, 15.05;  $\left. \begin{matrix} S \\ O \end{matrix} \right\}$ , 30.09; ash, 0.26.

The alcohol precipitate—

C, 40.25; H, 7.69; N, 9.60; S, 0.71; O, —; ash, 9.86.

These so different substances have no longer any specific action, and they appear to be products of the breaking up of a large molecule, the ferment molecule, or of the several molecules as the case may be.

As regards the loss of its activity by being heated to 70°, pancreatin agrees with emulsin, diastase, and pepsin, the *solutions* of which are likewise destroyed by this temperature. In the dry state, however, a heat of 100° has no effect.

Just as the higher and more complicated organisms, so also, in all probability, the simplest organisms have in their bodies, or in the interior of their cells, or their walls, substances which act as ferments, on the integrity and activity of which their life depends. This would agree with the fact of their being destroyed by a heat of 70° in water, while they may be heated in the dry state to 100° without suffering harm. Such facts are well known to naturalists.

Hüfner obtains similar ferments possessing both the diastatic power and the power of digesting fibrin, not only from the pancreas, but also from the salivary glands, from the lungs, and from rotten cheese. He is inclined to attribute their origin to oxidation of albuminoids, from which they differ chiefly in their percentage of oxygen.

D. F.

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**On the Value of Phenol as a Disinfectant.** By P. C. PLUGGE  
(Pfüger's Archiv. f. Physiologie, v, 538—565).

THIS memoir commences with some general observations on the processes of putrefaction and fermentation, the author inclining to the view that living organisms are the originators of these processes. Having regard to the fact that putrefaction, if not originated by living organisms, is always accompanied by the presence of these, it is important that such organisms should be rendered harmless, and this may be done in one of two ways. First, the conditions under which the organisms are developed may be so modified that innocuous forms of life alone may be produced, *e.g.*, by acidifying a liquid to a sufficient extent, only common forms of mould are developed, and the liquid is

decomposed by a process of oxidation. Secondly, the organisms may be altogether destroyed, and in disinfection this is the best and safest process. The author adduces experiments of his own to prove that phenol is the best known agent for achieving this. The essay is divided into three sections.

I. *The Antifermentative and Antiputrefactive Actions of Phenol.*—Starting from the fact that the intensity of putrefactive processes is always in direct relation to the amount of life present, it was sought to determine in what manner the lower organisms comport themselves towards phenol. But, inasmuch as the larger of these (paramecium, Euplotes, Colpoda, Opalina, &c.) are not proved to have any necessary connection with the putrefactive process, any conclusions drawn from this method of research are valid only on the supposition that the actions of phenol on the larger of the lower organisms and on the smaller (Vibrio, Bacteria, Monas, &c.) are analogous. This analogy of action was established by experiment, the power of resistance to the action of phenol varying only in quantity. The larger organisms in putrefying liquids were found to be more susceptible to the action of the disinfectant than the smaller.  $1-1\frac{1}{2}$  per cent. of phenol sufficed, however, to kill all the microscopic organisms in such a liquid, or to prevent their formation. The formation and continued life of fungi was also prevented by the same percentage of phenol in solution.

Alcoholic fermentation was found to be checked by phenol, and entirely arrested or prevented by 4 per cent. of the agent. The butyric fermentation in milk was also checked and stopped by  $\frac{1}{230}$  of phenol. As regards the glucosides, the statements of Crookes and others were confirmed, it being found that the actions of amygdalin and emulsin were uninfluenced by phenol. The saccharification of starch by saliva was, in opposition to previous statements, prevented either by the addition of large quantities of phenol, or by the prolonged action of the disinfectant, quantity and time being found to form important elements in the process. The peptonification of albumin was found to be checked by  $\frac{1}{500}$ , and entirely prevented by  $\frac{1}{200}$  of phenol. Some experiments made with the view of determining whether this was caused by the action of phenol on pepsin or on albumin, or on both, led to no decisive results, and the author reserves the solution of this question for further experiment.

II. *The value of Phenol as a Disinfectant in comparison with other Substances.*—Phenol is compared with the following substances:—ferrous sulphate, chloride of lime, chlorine, the permanganates, mineral acids, and quinine, and in each case the verdict is given unhesitatingly in favour of phenol. It was found that quinine hydrochloride did not entirely prevent the development of vibriones and monads in a mixture of sugar, milk, and water, nor prevent the butyric fermentation setting in. The salt was added to the experimental solution in the proportion of  $\frac{1}{150}$ .

III. *The Physiological Actions of Phenol.*—These were found to be similar to those of strychnine.

Phenol was found to be as active in the state of vapour in preventing the formation of living organisms as when used in solution.

T. S.



## Chemistry of Vegetable Physiology and Agriculture.

**On the Fermentation of Fruits** (Third Part). By J. BOUSSINGAULT (Ann. Chim. Phys. [4], xxvi, 362—375).

*Bilberries* (fruit of *Vaccinium Myrtillus*).—The berries were allowed to ferment spontaneously in a flask connected with a jar standing over mercury.

Bilberries.	Weight employed.	Containing		
		Sugar.	Alcohol.	Acid expressed as $H_2SO_4$ .
Before fermentation ....	gr. 9486·5	gr. 598·6	gr. 0·0	gr. 64·32
After       "       " ....	9166·3	0·0	239·63	64·88
Difference .....	—320·2	—598·6	+239·63	+0·56

The sugar, which, judging by its rotatory power, seemed to be wholly inverted sugar, should have given 305·9 of alcohol; only 239·63, or 78 per cent. of this was obtained.

These 239·63 grams of alcohol produced represent 229·3 of carbonic anhydride. The loss of weight after fermentation was 320·2, and there was, as shown in the table, but very inconsiderable increase in the proportion of acid.

*White Wine of Lampertsloch*.—Must of sp. gr. 10795 at 17° was taken and strained from the stalks, skins, and stones.

	Weight of must.	Sugar by copper test.	Alcohol.	Acid expressed as $H_2SO_4$ .
Before fermentation ....	gr. 9715·5	gr. 1688·46	gr. 0·0	gr. 39·74
After       "       " ....	8955·0	traces	781·41	47·82
Difference .....	—760·5	—1688·46	+781·41	+8·08

The alcohol obtained was about 91 per cent. of the amount which the sugar should theoretically have yielded.

The alcohol produced represents 747·8 of carbonic anhydride, the loss actually experienced being 760·5

By making a series of observations of the rotatory power of the must during the progress of the fermentation, it was found, as already shown by Dubrunfaut, that the dextroglucose is destroyed by fermentation before the lævulose.

*Honey*.—Fermented with washed beer yeast.

	Volume.	Weight.	Sugar by copper test.	Alcohol.	Acid expressed as $H_2SO_4$ .
	lit.	gr.	gr.	gr.	gr.
Before fermentation ..	3·845	4012·87	378·73	—	0·62
After            "        "	3·837	3823·00	traces	177·65	3·07
Difference .....	-0·008	-189·87	-378·73	+177·65	+2·45

The sugar should have produced 193·57 of alcohol. Calculating from the alcohol produced, 170 grams of carbonic anhydride should have been evolved. The actual loss incurred was nearly 190 grams.

W. A. T.

### Albuminoids and their changes during Germination. By PFEFFER (Versuchs-Stationen Organ, xv, 114—121).

THE author points out that in many papilionaceous plants, asparagine performs an intermediate part in the translocation of the albuminoids during germination, possibly acting in the same way as glucose does for the formation of non-nitrogenous substances.

In *Lupinus luteus* and other plants, asparagine and glucose appear together at the commencement of germination, and are confined to the same young organs and parts of the plant. Asparagine disappears at the first unfolding of the leaves. Albuminoids in being converted to asparagine must lose carbon and hydrogen, and in the reconversion these bodies must be obtained, probably from a non-nitrogenous constituent of the plant.

Seeds germinating in the dark consume a larger quantity of their non-nitrogenous matters than those germinating in the light, and so the substance necessary for the regeneration of albuminoids from asparagine is deficient. It may be in this way that asparagine accumulates in some plants grown in the dark.

E. K.

### Increase of Temperature during Germination, and its Causes.

By F. WIESNER. Versuchs-Stationen Organ, xv, 135—142).

EXPERIMENTS were conducted simultaneously on the increase of temperature and the amount of carbon dioxide evolved during the germination of hemp-seed. The seeds were kept moistened during the first 12 hours, with water at the same temperature as themselves.

The temperature of the seeds rose about 1° C. above the air, quickly after damping, and some time before carbon dioxide was evolved and continued to rise until the appearance of the cotyledons; the maximum excess over air-temperature was 7·5° C.; 166 seeds with a dry weight of 2·709 grams, gave off ·610  $CO_2$ , and produced plants weighing 1·364, showing a loss of 49 per cent. during germination. Similar experiments with barley produced like results; the greatest excess of

temperature over the air was  $4.7^{\circ}$  C. 63 grains of barley with a dry weight of 1.793 grams gave off 1.194  $\text{CO}_2$ , and produced plants weighing 1.431, showing a loss of 20 per cent.

The first rise in temperature is owing to a condensation of water in the tissues of the seed: for barley-meal and ground hemp-seed showed a similar rise when moistened, as did many other seeds.

That this rise is not due to oxidation was proved by moistening a mixture of ground seeds, from which no carbon dioxide was evolved during several hours, though the temperature rose.

E. K.

**Occurrence of Rubidium in Beetroot.** By E. PFEIFFER (Arch. Pharm. [2], cl, 97—102).

THE beetroot ash was obtained by evaporation of the liquid remaining after distillation of the alcohol obtained from the sugar syrup, and calcination of the residue. The average composition of the ash obtained from the beetroots of the north of France is the following:

Potassium carbonate.....	30 per cent.
Sodium carbonate.....	20    "
Potassium chloride.....	18    "
Potassium sulphate .....	9    "
Insoluble matter and moisture	23    "

Besides these substances, small quantities of iodine and bromine, and of rubidium, are contained in the ash. The above substances may be separated by crystallisation, or the potassium salts may be utilised first by converting them into the chloride and then into nitrate, by addition of sodium nitrate. After the separation of the greater portion of these salts by evaporation, &c., the rubidium may be precipitated from the diluted mother-liquor by addition of dilute solution of platinic chloride, or better by addition of a hot saturated solution of a potassio-platinic chloride. The precipitate obtained may be freed from the potassium salt by washing with water and then reduced in a current of hydrogen. The author estimates that the ash from the beetroot of the north of France contains about 1.75 gm. of rubidium chloride to the kilogram of ash. From this it follows that 1 hectare of land yields about 255 grams of rubidium chloride to every crop of beetroot. The rubidium chloride contained a trace of caesium, but no lithium was found in the ash. Tobacco from the same region contains potassium, rubidium, and lithium, and traces of sodium, whilst rape-seed contains only potassium and sodium, but neither rubidium nor lithium.

A. P.

**Distribution of Atropine in the Leaves and Root of Belladonna.** By M. LEFORT (Pharm. J. Trans. [3], ii, 1029).

LEAVES from cultivated plants gathered in May, before flowering, and others gathered in August, after flowering, yielded the following



quantities of atropine. In each case the atropine is given in 100 grams of the dry substance—

Experiment.	May leaves. gram.	August leaves. gram.
1 .....	0·418 .....	0·457
2 .....	0·405 .....	0·443
3 .....	0·421 .....	0·467
4 .....	0·392 .....	0·482

Leaves gathered in July from cultivated plants, and others from wild plants, gave results as follows :—

Experiment.	Cultivated leaf. gram.	Wild leaf. gram.
1 .....	0·470 .....	0·459
2 .....	0·485 .....	0·477

The leaf is therefore less rich in atropine in the spring than after the floral organs have faded, and there is no appreciable difference whether the plant grows wild or is cultivated.

Roots of various ages gave the undermentioned results :—

Experiment.	Root two to three years old. gram.	Root seven to eight years old. gram.
1 .....	0·4718 .....	0·2541
2 .....	0·4886 .....	0·3128

Though the root is occasionally richer in atropine than the leaf, yet it is much more variable in composition, and hence the leaf will have more uniform therapeutic properties.

J. B.

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**Bark of the Juglans Cinerea.** By C. O. THIEBAUD (Pharm. J. Trans. [3], ii, 1033).

THIS bark yields bitter extractive, a large amount of oily matter, an acid which the author has named *juglandic acid*, an acid crystallising in colourless tabular crystals, and a volatile acid, but no alkaloids or tannin. Juglandic acid crystallises in short acicular crystals of a bright orange-yellow colour, and appears to be related to chrysophanic acid.

J. B.

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**Some Constituents of Ericaceous Plants.** By J. OXLEY (Pharm. J. Trans. [3], ii, 1050).

AMONG the organic constituents of *Gaultheria procumbens* and *Epigaea repens* are arbutin, ursone, ericolin, tannic acid, a principle analogous to gallic acid, formic acid (in *Epigaea*), grape-sugar, gum, and colouring matter. Arbutin, ursone and ericolin have previously been found in

*Ura ursi* and *Chimaphila umbellata*, and therefore appear to be common to plants of the Ericaceae order.

J. B.

### On the Nature of Silicium Compounds Occurring in Plants.

By A. LADENBURG (Deut. Chem. Ges. Ber., v, 568).

NOT improbably part of the silica found in plant-ashes arises from the destruction of silico-organic compounds; and the silica occurring in living plants may have a similar origin. Cellulose from filter-paper treated with dilute nitric acid and potash-solution to eradicate soluble and decomposable silicates, still gave an ash containing 40 per cent. of silica with much lime and iron oxide. Swedish filter-paper, dissolved in cuprammonia solution and precipitated by hydrochloric acid, still gave 0.11 and 0.16 per cent. ash, whereof one-third was silica; so that a small amount of silicates appears to exist in the purest cellulose.

*Equisetum arvense* gave 20 per cent. of ashes, of which one-fourth was silica; but when it was previously warmed with strong hydrochloric acid, and then with potash, the ash fell to 16 per cent., of which only one-tenth was silica; in the alkaline extract from this plant, a carbonaceous silicic acid (like silico propionic acid) was sought for, by precipitation with hydrochloric acid, evaporation of filtrate, solution of residue in potash, and dialysis of the solution: the remaining liquid left on evaporation a nearly pure silica, giving only 1.0 per cent. of carbonic acid on combustion with copper oxide.

C. R. A. W.

### The Oxidation-blue of *Boletus Cyanescens*, *B. Luridus*, &c.; compared with a similar Product derived from Phenol. By

T. L. PHIPSON (Chem. News, xxv, 301).

THE intense blue colour produced by the addition of calcium hypochlorite to an alcoholic solution of the yellowish colouring matter of *Boletus luridus*, &c.; and the blue tint assumed by a freshly cut surface of *Boletus* when exposed to the air is, in the author's opinion, to be attributed to the oxidation of aniline naturally present in the tissues of these fungi. The supposition is based upon the similarity of the colour developed in the following reaction:—

A small quantity of phenol is dissolved in methyl alcohol saturated with ammonia, and calcium hypochlorite is cautiously added until a blue colour is produced. The diluted aqueous solution of the colour, when acidified by hydrochloric acid, first assumes a reddish tint, then gradually deposits a resinous substance, and becomes yellow. This yellow solution in presence of ammonia, takes a blue colour in a very few minutes by exposure to the air.

The colour thus artificially prepared, is very similar in tint to that produced by the oxidation of the extractive of several species of the above-mentioned fungi.

J. W.

**Cultivation Experiments with Flax.** By A. SCHISCHKIN (Versuchs-Stationen Organ, xv, 126—133, and 161—170).

THE author determined the dry substance and oil in the various parts of the plant at three stages of its growth. The seed (American white-blossoming linseed) was sown on May 1 in a rich soil. On June 7 the first sample was taken; the plants had then reached the middle internode. On June 15 the second sample was taken; blossoming had then commenced. On July 28 the final sample was taken; the plants were then fully ripe. The following table shows the rate of increase of the dry matter and oil during growth, the amount in the full-grown plant being taken as 100\* :—

	Dry matter.	Oil.	Percentage of oil in dry matter.
First period .....	2·29	1·73	5·20
Second period .....	23·90	17·84	5·67
Third period.....	73·81	80·43	7·27
	100·00	100·00	

The upper parts of the plant are richer in oil than the lower parts. The percentage of oil in the lower parts diminishes as growth proceeds; the absolute amount, however, increases. The leaves are much richer in oil than the stem. The author compares his results with those obtained by Arendt with oats: the development of starch in the later growth of the oat corresponds with the production of oil in the case of flax.

Flax was grown in pots with soil variously manured. The soil was a poor loam, containing in 100 parts but ·156 CaO, ·098 K<sub>2</sub>O, and ·039 P<sub>2</sub>O<sub>5</sub> soluble in hydrochloric acid. Each pot held 3,500 grams of soil, and was planted with 35 flax seeds. The plants grew in the open air. The flax receiving phosphates bloomed the earliest, that manured with ammonium sulphate the latest. The results are shown in the following table, in which the produce of the unmanured pot is taken throughout as 100 (save in the case of the right-hand column), and the produce by manuring is stated in relation to this standard :—

\* The figures here given are those quoted by the author in the body of the paper; the more detailed figures supplied by the author's table (S 132) unfortunately do not substantiate them: thus, calculation from the detailed table gives 42·48 as the increase of dry matter in the third period.—R. W.



Manures.	Weight of crop.	Length of stalks.	Weight of stalks.	Weight of branches.	Weight of seed.	Weight of oil in seed.	Per cent. oil in seed.
18 grm. CaO .....	140·9	88·0	153·2	219·7	117·1	116·3	35·27
33 grm. CaCO <sub>3</sub> .....	135·6	95·8	116·0	255·9	135·4	133·1	34·90
40 grm. CaCl <sub>2</sub> .....	75·7	109·3	75·4	57·0	85·2	87·6	36·46
43 grm. CaSO <sub>4</sub> .....	127·2	108·9	132·3	129·9	125·9	129·4	36·46
53 grm. CaN <sub>2</sub> O <sub>6</sub> .....	150·3	100·9	140·9	207·4	153·9	152·3	35·15
31 grm. Ca <sub>3</sub> P <sub>2</sub> O <sub>8</sub> .....	164·1	106·5	154·3	170·0	176·5	159·2	32·03
50 grm. Ca <sub>3</sub> P <sub>2</sub> O <sub>8</sub> .....	195·0	78·7	149·0	436·1	197·1	170·0	30·65
48 grm. KCl .....	92·4	88·0	89·1	146·1	84·3	83·7	34·97
54 grm. K <sub>2</sub> SO <sub>4</sub> .....	85·8	78·7	102·1	82·7	67·3	69·9	36·84
54 grm. K <sub>2</sub> SO <sub>4</sub> + 38 grm. MgSO <sub>4</sub> .....	126·6	86·6	119·6	236·6	114·3	108·0	33·66
55 grm. KNO <sub>3</sub> + 4 grm. Ca <sub>3</sub> P <sub>2</sub> O <sub>8</sub> .....	130·9	101·8	141·4	219·1	92·0	87·0	33·55
44 grm. Na <sub>2</sub> SO <sub>4</sub> .....	79·3	111·1	104·1	44·9	83·5	95·0	40·38
38 grm. MgSO <sub>4</sub> .....	98·4	101·8	105·4	68·5	106·8	112·2	37·27
42 grm. (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> .....	111·9	100·5	115·5	181·2	88·1	85·8	34·84
No manure .....	100·0	100·0	100·0	100·0	100·0	100·0	35·51

Experiments were made as to the best time of harvesting flax. A portion of a uniform crop, grown in pots, was harvested when the seed-capsules began to turn brown, and only one-third of the stalk had become yellow; the remainder was harvested 17 days later, when complete ripeness had been reached. There was a considerable gain in weight of the stalks and branches during the 17 days of extra growth, but the fibre was of inferior quality. The seed gained very little weight during the same period, but both its absolute and percentage contents of oil increased very distinctly. The same increase of oil in the seed was observed in a portion of the unripe crop which after harvesting was kept 14 days before the seed was removed; the seed in this case lost weight, while it gained in oil; there was apparently, therefore, a transformation of the contents of the seed into oil.

R. W.

**Field Experiments on Potatoes.** By A. VOELCKER (Royal Agric. Soc. Journ. [2], vi, 392—415; Chemischer Ackersmann, 1871, 47—56).

MANURING experiments on potatoes in 1867-1869, show that on light soils a mixture of mineral superphosphate, crude potash-salts and ammonium sulphate produces very beneficial results; on stiff soils nitrogenous manures have little effect. Further proof is given that manuring with common salt tends to decrease the yield.

Analyses, communicated by A. Stockhardt, of potatoes grown in eight different years, show that those manured with salt invariably contain less starch than those unmanured, the decrease being from 10 to 20 per cent. of the starch; the same effect is produced when the salt is mixed with other manures.

Under the microscope the cells are seen to be very sparingly filled

with starch-grains. Unmanured potatoes contained 43 per cent. of sodium chloride in the dry substance, and those which had received a small dressing of common salt 1.34 per cent.

E. K.

**Digestion of Clover.** By E. WOLFF (Chemischer Ackersmann, 1871, 56—62).

EXPERIMENTS on the digestion of green clover and clover-hay by sheep. During the four weeks from the beginning to the end of flowering, the digestibility of all the constituents of green clover decreased; of the total dry substance the decrease was from 69 to 56 per cent.; organic substances from 71 to 58, albuminoids from 75 to 58, non-nitrogenous extractive matters from 78 to 70, crude fibre from 56 to 38, and fatty matters from 66 to 44 per cent. The digestibility of clover-hay is but slightly less than that of green clover cut at the same period of growth.

E. K.

**Nutritive Value and Composition of Roots.** By E. SCHULZE (Versuchs-Stationen Organ, xv, 170—181).

A PART of the nitrogen of mangolds and other feeding-roots exists in the form of ammonia-salts, asparagine, and nitrates. In calculating the feeding-value of roots, the whole of the nitrogen is usually reckoned as albuminoids, which are thus estimated in excess of the truth. Ammonia forms 0.08—0.22 per cent. of the sap of mangolds. The amount of asparagine present is unknown. Nitrates are always present, and rise frequently to large amounts. In analyses of 17 samples of mangolds, turnips, and sugar-beet, grown on various soils, the nitrogen as nitrates varied from 1—31 per cent. of the total nitrogen. The mangolds generally contained the largest quantity of nitrates. High nitrates are associated with high albuminoids, and generally with a high ash. A crop of mangolds rich in nitrates was examined at intervals during the second year's growth; the percentage of nitrates in the dry substance increased somewhat, but irregularly, up to the formation of seed; on the ripening of the seed the nitrates greatly diminished. The author determines nitrates by exhausting the dry substance with alcohol, and then treating the alcoholic solution by Schlösing's method.

The proportion of sap to mark is generally higher when determined by Grouven and Stammer's method, than when the pulped root is exhausted with water and the residual mark weighed. In Grouven and Stammer's method the dry matter in the sap and in the whole root is determined, and the proportion of sap to mark is found by the formula

$$x = \frac{100(100-a)}{100-b}, \text{ where } a \text{ is the percentage of dry matter in the whole}$$

root,  $b$  that in the sap, and  $x$  the percentage of sap in the root. The difference between the two methods is due to the difficulty of drying the root and sap completely; the difficulty is greater in the case of the sap, the residue from which requires 13 hours' drying at 100° in a stream of

hydrogen before it ceases to lose weight. Serrurier suggests a previous mixture with alcohol to facilitate the drying of saccharine fluids. The author regards the direct weighing of the mark as the simplest mode of analysis. Both methods give the same result when properly conducted.

R. W.

**The Nutritive Value of Meadow Grass.** By H. SCHULTZE, E. SCHULZE, and M. MÄRCKER (Ann. d. Landwirthschaft, 1871, 130—141).

It is known that pastures often differ considerably in their fattening properties; it is also well known that hay has a lower nutritive value than fresh grass. The authors show that these facts are in agreement with the composition and ascertained digestibility of the various fodders. The principal analyses are given below. No. 2 is from the same field as No. 1, but from a part irrigated with liquid manure in the preceding winter. No. 3 is from the famous Oldenburg marshes. From all the samples of grass the weeds were picked out and only clover and grass retained; \* from No. 3 the hard stalks avoided by animals were also removed. The samples were tried at 50°.

No.	100 parts of dry fodder contain :—	Mineral matter, minus CO <sub>2</sub> .	Total albuminoids.	Non-nitrogenous extractive matter.	Crude fat.	Woody fibre (purified).	Percentage of albuminoids, soluble.	Per cent. of non- nitrogenous extract, soluble.
1 {	Grass, 2½ inches high,	7·65	13·38	57·01	4·82	17·14	40·7	62·0
May 26 .....								
2 {	Grass, 6 inches high,	8·19	19·34	49·04	5·24	18·13	39·3	50·2
May 26 .....								
3 {	Grass, rich pasture, end	10·22	19·94	43·83	3·75	22·26	47·5	52·1
of June .....								
4 {	Hay, from second cut	9·22	16·11	48·58	3·11	22·98	26·4	48·6
of grass .....								
5 ..	Hay, fair quality, 1867 ..	6·55	11·40	47·90	3·03	31·10	32·5	47·9
6 ..	Hay, fair quality, 1868 ..	6·92	10·60	52·88	2·60	27·00	25·8	45·1

It appears that grass differs from hay (the fully-matured product) by containing more of mineral matter, albuminoids, and fat, and less of woody fibre; while both the albuminoids and extractive matter of grass are present in a more soluble form than in hay. Hay made from the autumnal cutting approaches grass in composition.

The previous investigations of E. Wolff on grass and red clover, and of Ritthausen on Lucerne, show the same alteration of composition as maturity advances. Their results were in brief as follows :—

\* The proportion of clover to grass is unfortunately not mentioned.—R. W.



	Grass.		Red clover.				Lucerne.		
	Young.	Older.	Young.	June 13.	June 23.	July 20.	April 24.	May 22.	July 3.
Ash .....	9·4	8·5	9·8	7·2	5·8	5·6	8·6	9·7	7·2
Albuminoids.	22·0	16·3	21·9	13·8	11·2	9·5	23·7	21·9	14·8
Woody fibre.	18·5	21·3	24·7	32·8	32·9	41·7	18·3	22·6	40·4

The authors analysed the ash of the various samples of grass and hay. The ash of the grass contained much more potash and phosphoric acid, and less silica than the ash of the hay: this agrees with the early results of Way and Ogston. The ash of the after-grass differed both from grass and summer hay by containing less potash and an excess of soda, lime, and chlorine.

Immature grass being richer in food-constituents, and containing them in a more soluble form, it becomes highly probable that it is more digestible, and has a greater feeding value than hay. The authors refer to the feeding experiments of Schulze and Märcker (see vol. ix, 1074, of this *Journal*), proving that autumnal hay is more perfectly assimilated by sheep than summer hay, and argue from a comparison of the above analyses that grass would be still more digestible.

R. W.

### Composition of Pulse from South Russia, and of the Legumin obtained therefrom. By R. POTT (Versuchs-Stationen Organ, xv, 214—217).

THE samples of pulse dried at 100° had the following percentage composition:—

No.		Albumi- noids.	Starch, &c.	Crude fat.	Crude fibre.	Ash.	Nitro- gen.
1	Peas from Cherson.....	26·40	66·01	2·67	4·13	2·79	4·40
2	Chickling vetches ( <i>Lathyrus sativus</i> ) from Cherson .....	29·28	60·82	2·11	4·35	3·44	4·88
3	Chickling vetches from Jekaterinoslaw .....	26·46	65·07	2·25	3·53	2·69	4·41
4	Beans from Jekaterinoslaw ...	26·40	62·64	2·78	4·20	3·98	4·40
5	Lentils from Cherson.....	25·80	64·81	2·67	3·95	2·77	4·30
6	Lentils from Jekaterinoslaw...	28·56	62·33	2·57	3·68	3·12	4·76

In the district of Poppelsdorf (where the author resides) the percentage of nitrogen in peas varies from 3·39—4·41, in beans from 3·17—5·11, and in lentils from 4·00—4·53.

Legumin was prepared by Ritthausen's method from samples 1 and 3; the mean composition of the ash-free legumin was as follows:—

	C.	H.	N.	O.	S.
Prepared from Sample 1 ..	51·67	6·72	16·88	24·26	0·47
Prepared from Sample 3 ..	51·98	7·00	16·95	23·60	0·47

This composition is quite similar to that obtained by Ritthausen, and also agrees with the results obtained from pulse grown at Popplesdorf.

R. W.

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**Composition of the Ash of Hard and Soft Wheat.** By R. POTT  
(Versuchs-Stationen Organ, xv, 217—222).

THE gluten of hard glossy wheat is easily separated by washing with water; the gluten of soft mealy wheat is not easily separated. The author examined the ash of four specimens of each kind of wheat in the hope of throwing light on the subject, but concludes that there is no relation between the constituents of the ash and the property in question. The figures show, however, that hard wheat yields on an average more ash than soft wheat, and that the ash contains more phosphoric acid and less potash than that from soft wheat; and though in one case the latter relation is decidedly reversed, it is only so with the whole grain, the ash of the flour conforming plainly to the rule. The composition of the ash thus corresponds with the respective preponderance of gluten and of starch. Church found that the translucent horny grains picked from a sample of wheat contained about one-third more nitrogen than the soft mealy grains picked from the same sample.

R. W.

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**Composition of the Seed-shells of White Clover.** By SENFF  
(Chemischer Ackersmann, 1871, 126).

A CLEAN, air-dried sample, analysed by Henneberg's method, gave the following result:—

Water .....	11.41
Albuminoids .....	18.35
Soluble carbo-hydrates .....	36.83
Crude fat .....	3.09
Crude fibre .....	22.42
Ash.....	7.90

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100.00

R. W.

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**Clover Sickness.** By J. H. GILBERT (Journ. Roy. Horticultural Soc., 1872, 86—95).

IF red clover be repeated at short intervals on the same land, the crop soon fails, and the land is said to be "clover sick." After changing the crop for some years, the land regains its power of growing clover. Mr. Lawes and the author have made field experiments since 1849 upon the cause and cure of clover sickness, but as yet with only negative results. When land is not clover sick, manuring with potash salts and phosphates considerably increases the crop, but this manure

does not prevent clover sickness. All applications of mineral, organic, and nitrogenous manures have failed in preventing clover sickness. The field is, however, at present rather less clover sick on those parts which received most of these three descriptions of manure in bygone years. In 1864, and again in 1867, portions of the field were deeply dug, and a mixture of cinereal manures and nitrate of soda incorporated with the soil, in some cases from a depth of 3 feet upwards, but no benefit as yet appears from this manuring of the subsoil. In striking contrast to these failures, red clover has grown luxuriantly on the soil of an old kitchen garden since 1854, and shows no signs of falling off. In 17 years there has been removed from this plot in the form of clover more than 1 ton of potash, and  $1\frac{1}{2}$  ton of nitrogen per acre, without any manure being applied.

These facts offer a wide field for hypothesis. The author thinks that the restorative effect of time may perhaps be owing to the formation and distribution of nitrates and salts of organic acids, while the cinereal plant-food may also assume a condition more favourable to assimilation.

R. W.

### Absorption of Ammonia from the Air by Humus. By P. BRETSCHNEIDER (Chemischer Ackersmann, 1871, 187—190).

Large quantities of humus being required for the experiments, it was prepared artificially by boiling sugar with dilute sulphuric acid. The substance obtained contained, when dried at  $110^{\circ}$ , C. 60.397, H. 4.502, O. 35.034, N. .025, ash .042. The author calls this body *ulmin*; the composition is, however, that of humic acid. The experiments were made in four metal dishes, each 6 inches deep, and exposing a surface of 1 square foot. Each vessel contained 15 kilograms of quartz-sand moistened with 3.55 kilograms of water. One vessel was without humic acid, the others contained respectively 1, 3, and 5 per cent. of the weight of the sand. The vessels were exposed freely to the open air for one year, but sheltered from rain and insects; the evaporated water was from time to time replaced. At the end of the experiment the increase of nitrogen with 1 per cent. humic acid was .069 gram, with 3 per cent. humic acid .239 gram, and with 5 per cent. humic acid .454 gram; or, calculating the results for an acre of surface, the increase was respectively 6.24, 21.72, and 41.14 pounds of nitrogen. It is to be observed that the absorption of nitrogen rises more rapidly than the proportion of humic acid present. The author does not show that the nitrogen was absorbed as ammonia.\*

R. W.

### Influence of Ammonium Sulphocyanate on Plant Growth. By C. SCHUMANN (Versuchs-Stationen Organ, xv, 230—231).

A CHEAP "brown sulphate of ammonia" received from England was found to contain 30.4 per cent of nitrogen, and further investigation

\* Compare Deherain's experiments, page 165 of this volume..



proved it to consist principally of ammonium sulphocyanate. Experiments were made with it before it was employed as manure. When it was applied to a meadow at the rate of  $1\frac{1}{2}$  cwt. per acre, the grass partly died, and the first cutting was entirely lost. When it was mixed with superphosphate and applied to potatoes the result was decidedly injurious, the produce being two-thirds less than the general crop.

R. W.

**Crude Ammonia.** By M. MÄCKER (Versuchs-Stationen Organ, xv, 233—237).

THE author points out that the crude ammonia salts resulting from the purification of coal gas are frequently quite unfit for use as a manure. The presence of ferrous salts and sulphocyanates is especially objectionable. As cyanogen is always present, ammonia should be actually determined in analysis, and not merely the total nitrogen.

R. W.

## Analytical Chemistry.

**Contributions to Gas Analysis.** By E. LUDWIG (Ann. Chem. Pharm., clxii, 53—60).

IN gas analysis we frequently employ balls made of the dioxides of manganese or lead, or of lead phosphate, which, however, are extremely liable to break, especially after they have been soaked with phosphoric acid. The author recommends mixing plaster of Paris with those absorption agents which are not fusible, making the mixture into a paste with water, and pressing it round the platinum wire into the mould, the inside of which has been oiled. A hard ball, firmly attached to the platinum wire, is thus formed in a few minutes; but in order to prevent absorption of carbonic acid by the physical action of the pores, this ball has to be treated with phosphoric acid.

For the absorption of *hydrogen sulphide* the author recommends balls prepared by mixing two parts of lead phosphate with three parts of plaster of Paris.

The following are the results of some analyses in which balls of lead phosphate have been employed:—

### *Mixture of Carbon Dioxide and Hydrogen Sulphide.*

	Taken.	Found.	Taken.	Found.	Taken.	Found.
	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
Carbon dioxide.....	69·60	69·79	76·11	76·13	54·25	54·28
Hydrogen sulphide.....	30·40	30·21	23·89	23·87	45·75	45·72

*Mixture of Hydrogen, Carbon Dioxide, and Hydrogen Sulphide.*

	Taken.	Found.	Taken.	Found.	Taken.	Found.
	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
Hydrogen .....	27·89	27·80	29·39	29·38	34·33	34·22
Carbon dioxide .....	26·00	26·26	29·35	29·38	25·84	25·66
Hydrogen sulphide ....	46·14	45·94	41·26	41·24	40·19	40·12

For the absorption of *sulphur dioxide*, balls consisting of plaster of Paris and an equivalent of manganese or lead dioxide give good results, as the following analyses show :—

*Mixture of Sulphur Dioxide and Carbon Dioxide.*

	Taken.	Found.	Taken.	Found.	Taken.	Found.
	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
Carbon dioxide .....	61·04	61·22	67·54	67·23	61·80	61·73
Sulphuric dioxide .....	38·96	38·87	32·46	32·77	38·20	38·27

For the determination of carbon monoxide, balls of plaster of Paris steeped in a mixture of one volume of saturated chromic acid solution and two volumes of water are left twelve hours in the mixture of gases to be examined. The carbonic acid formed has to be determined by absorption with potash.

The mould used for the preparation of the balls must in this case have its inside covered with a layer of paraffin, as oil would be acted upon by the chromic acid.

The accuracy of the method can be seen from the following results :—

*Mixture of Carbon Monoxide and Hydrogen.*

	Taken.	Found.	Taken.	Found.
	c.c.	c.c.	c.c.	c.c.
Hydrogen .....	64·86	65·34	68·26	68·07
Carbon oxide .....	35·14	34·66	31·79	31·93

R. S.

### Analytic and Pyrometric Estimation of Graphites. By CARL BISCHOF (Dingl. Polyt. J., cxxix, 139—152.

THE author points out the uncertainty attending the chemical examination of the various specimens of graphite used in the lead pencil manufacture. He considers that the determination of the carbon alone is an insufficient guide to the quality of the graphite; that the other constituents must be also determined, especially alumina and silica; and that the relation of these to one another, and to the quantity of silicic

acid and aluminium silicate used in the pyrometric trials for the fusion of the graphite is of the utmost consequence. An exact chemical analysis should always be associated with a practical pyrometric determination of the value of the specimen.

The pyrometric estimation is made by exposing finely powdered graphite, mixed with  $12\frac{1}{2}$  per cent. then with 25 per cent. clay in a closed crucible, to a temperature equal to that at which platinum melts, the appearance being noted, the heat is increased, until fusion occurs and the fused mass is examined. The power of withstanding fusion is found to be less in a graphite containing a large amount of alumina than in one containing less of that substance. A determination is also made by carefully mixing finely powdered graphite with 20—40 per cent. silica, exposing the mixture to the heat at which cast steel melts, and noting the appearance of the mass.

M. M. P. M.

### Separation of Phosphoric Acid, Ferric Oxide, Alumina, Lime, and Magnesia. By THOMAS R. OGILVIE (Chem. News, xxv, 277).

It is generally known that Sonnenchein's method of separating phosphoric acid as phospho-molybdate of ammonia, cannot be depended upon, excepting when the quantity of phosphoric acid to be determined is very small. The method is therefore seldom adopted for the analysis of phosphatic minerals. The experiments of the author bearing upon this subject show that the method is *not* unfitted for the examination of such minerals as apatite, coprolite, &c., and that a quantity of substance may be employed containing at least as much as 0.3 gram. of phosphoric acid, without affecting the accuracy of the estimation. He is also of opinion that under all circumstances the results are more to be relied upon than those obtained by other processes in more common use, which involve the separation of the phosphoric acid in presence of organic salts, such as oxalate or citrate of ammonium.

No new practical details are offered respecting the separation of phosphoric acid or the alkaline earths. As regards the separation of ferric oxide and alumina, the author considers the method proposed by Fresenius as too troublesome and protracted; he prefers precipitating the mixed oxides by ammonia, and separating any adhering molybdic acid by redissolving them in nitric acid, and precipitating them a second time. In this manner he has obtained perfectly satisfactory results.

The following test analyses show the accuracy which may be obtained:—

	Used.	Found.	Used.	Found.
P <sub>2</sub> O <sub>5</sub> .....	0.1984	0.1982	0.0397	0.0409
Fe <sub>2</sub> O <sub>3</sub> .....	0.030	0.0312	0.150	0.1485
Al <sub>2</sub> O <sub>3</sub> .....	0.020	0.0208	0.100	0.1015
CaO .....	0.3298	0.3282	0.1319	0.1310
MgO.....	0.0570	0.0555	0.114	0.1146

J. W.



**On a New Method of Determining Ozone Quantitatively.**By P. THÉNARD (*Compt. rend.*, lxxv, 175—177).

THE process recommended by M. Thénard, for determining the quantity of ozone present in a volume of oxygen depends upon the oxidising action which ozone exerts upon arsenious acid, the ozone itself being meantime reduced.

The method of procedure is as follows:—Into a measured flask containing the ozonised oxygen, 10, 12, 15 c.c., according to circumstances, of standard solution of arsenious acid in hydrochloric acid, are introduced. The solution is made on Gay-Lussac's method, and is of such a strength that it requires about 0.1 milligram of oxygen to convert the arsenious into arsenic acid. After brisk agitation at short intervals, 30 c.c. of sulphuric acid solution are added, and the quantity of arsenious acid unconverted by the ozone is determined by means of standard solution of potassium permanganate. The subsequent calculations are simple.

In order to be confident in the process now proposed, it was necessary to ascertain the manner in which the result was affected by the presence—1. of nitric acid; 2. of nitrous acid; 3. of peroxide of hydrogen. These appeared to be the only bodies likely to be present with the ozone, which might react upon the arsenious acid and permanganate.

It was found that the presence of a considerable quantity of nitric acid does not affect the test in the least. On mixing with the arsenious acid solution a quantity of nitrous acid, it was found to oxidize itself at the expense of the permanganate; and thus the presence of this body would lower instead of raising the apparent quantity of ozone in an analysis. Peroxide of hydrogen was also found to give a similar result. It also decolorizes the permanganate solution, and its presence would therefore diminish the apparent quantity of ozone.

Finally, owing to an observation that certain bodies exposed to the action of ozonized oxygen continue to exhibit reactions as if ozone were present after all the ozone, so far as can be detected with test-papers, is destroyed, the author made comparative experiments to determine whether the apparent action of ozone upon arsenious acid increases with the time. He found that this is not to be the case. In a set of ten flasks, five of which were tested after a few minutes, and the other five after five hours' waiting, the action of the ozone upon the arsenious acid was the same.

J. T. B.

**Action of Potassium Permanganate on Peroxide of Hydrogen under the Influence of a Freezing Mixture.** By P. THÉNARD (*Compt. rend.*, lxxv, 177).

M. THÉNARD describes an experiment which he was led to make during the investigations connected with the subject of the preceding paper. He has shown that peroxide of hydrogen has no action on arsenious acid. Whence comes its action on potassium permanganate? Brodie has observed that under ordinary circumstances the disposable

oxygen of both the reacting substances becomes free, and is given off with violence. Under the influence of a freezing mixture, however, this is not the case; the permanganate, indeed, is still decolorized, but the oxygen remains combined so long as the temperature is low. When, however, the temperature rises, the oxygen is given off. The author reserves the discussion of this experiment for a future occasion.

J. T. B.

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**Second Contribution to the determination of Nitrates, Nitrites, and Hydrogen Peroxide by Solution of Indigo.**

By H. STRUVE (Zeitschr. Anal. Chem., xi, 25—29).

THE statements of Professor Goppelsröder and Dr. Trommsdorff, respecting the titration, by indigo-solution, of nitrates in presence of nitrites being contradictory, the author made several experiments which showed that the amount of solution required by mixtures, was nearly equal to the sum of the quantities which each constituent required separately.

A. T.

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**Estimation of Nitric Acid in Potable Waters.** By THOS. P. BLUNT (Chem. News, xxv, 205).

THE following process for the estimation of nitric acid in potable waters is offered as being specially applicable in those cases in which the water has been previously examined by Wanklyn and Chapman's method.

When the final distillation with hydrate and permanganate of potassium is completed, the residue is, if necessary, transferred to a smaller retort, and the permanganate carefully reduced by the successive addition of small quantities of sodium sulphite. Some aluminium foil, weighing eight or ten times as much as the nitric acid judged to be present, is next introduced, and the evolution of hydrogen having ceased, distillation is proceeded with, the distilled product being received in a small flask partially filled with pure water free from ammonia. The distillation may be interrupted when two-thirds of the liquid has passed over; the distillate is then transferred to a measuring flask, an aliquot part taken, and the ammonia estimated by the Nessler test in the usual manner.

The addition of a small quantity of recently ignited charcoal powder will be found very successful in preventing the violent bumping which so frequently occurs during the ebullition of caustic alkaline liquids.

The process appears to be a special application of Schultze's "aluminium method."

J. W.

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**Precipitation of Phosphoric Acid.** By L. BRUNNER (Zeitschr. Anal. Chem., xi, 30—32).

THE author considers it absolutely necessary that the precipitation of phosphoric acid by ammonio-magnesium sulphate should be effected in

the cold. Two equal portions of hydrochloric acid solution of bone-ash were taken, and after the iron and calcium had been separated, the one was precipitated at a temperature of  $60^{\circ}$ — $70^{\circ}$ , and the other at about  $20^{\circ}$ , when it was found that the first gave 30.15, the second 28.9 per cent. of  $P_2O_5$ , the result in the first case being 1.25 per cent. too high.

A. T.

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**Action of Ether on Iodides.** By E. FERRIÈRE (Compt. rend., lxxiv, 1106).

WHEN an iodide mixed with starch-paste is treated with ether, iodine is set free with a blue coloration, at once if concentrated, slowly if dilute. By filtration and further addition of ether and starch, the iodine can finally be completely removed. The reaction, which applies equally well to natural iodine-waters, but does not affect chlorides and bromides, is probably due to the formation, and subsequent decomposition, of ethyl iodide.

C. G. S.

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**A Singular Barium Reaction.** (Dingl. Polyt. J., cciii, 500.)

IF fresh spring water containing calcium sulphate be shaken with excess of barium carbonate, and filtered after a short time, the filtrate when tested with barium chloride, is found to contain no more sulphuric acid, but a considerable quantity of barium carbonate, held in solution by the carbonic acid contained in the fresh spring water.

On adding a fresh quantity of spring water to the filtered water containing barium, turbidity is produced, some barium sulphate being precipitated. The turbid solution is now filtered, and to one portion of the clear filtered liquid sulphuric acid is added, and to another barium chloride, when in both cases precipitates are of barium sulphate are formed. Thus it appears that in neutral solutions sulphuric acid and barium can exist together, without precipitation of barium sulphate taking place, and this has actually been found to be the case in many mineral springs.

W. S.

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**The Logwood Test for Alum in Bread.** By GEORGE E. DAVIS (Chem. News, xxv, 207).

THE writer, knowing the criticisms which have been passed upon the use of logwood as a reagent for the detection of alum in bread, thought it worth while to make some special experiments respecting the action of certain other salts upon the colouring matter of this substance. They may be briefly summed up as follows:—

Solution of alum communicates a purple-red colour to a dilute infusion of logwood, identical with that of a solution of potassium permanganate. The addition of a small quantity of sulphurous acid does not destroy this colour, but slightly weakens it. Solutions of sodium tartrate, phosphate and carbonate, give a red-brown coloration; the colour in the case of the phosphate slightly inclining to purple.



The original straw-yellow tint is in each case instantly restored by the addition of sulphurous acid.

A trace of caustic ammonia also gives a red-brown colour, which upon further addition turns violet and violet-blue: on neutralising the alkali with an acid, the straw-yellow returns.

Iron and copper salts, reacting with the tannin of the logwood, communicate a purple or blue colour to the infusion, which is also destroyed on the addition of sulphurous acid.

A decoction of potatoes gives to an infusion of logwood, a colour similar to that produced by sodium phosphate. It differs materially from the coloration produced by alum, and is unstable in the presence of an acid.

The author does not state that the logwood test for alum may be relied upon, but he would seem to imply that with a certain amount of experience, the indications which it affords are not to be considered as altogether fallacious.

J. W.

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**Application of the Sprengel Mercurial Pump to the Estimation of Carbon in Iron and Steel.** By JOHN PARRY (Chem. News, xxv, 301).

THE finely divided metal is digested in solution of copper sulphate, and the precipitated copper mixed with the carbon, is filtered, and washed through asbestos. The dried residue is mixed with copper oxide, placed in a combustion tube, and the drawn out end connected with the Sprengel pump.

A vacuum having been formed, the combustion is proceeded with, and the carbonic anhydride subsequently pumped out and measured in a calibrated glass tube.

The accuracy of the process is shown by comparison in the following experiments:—

	Ordinary combustion with oxygen.	Combustion in vacuo.
1 Grey pig iron....	3.27	3.206
2. Ditto ....	3.60	3.654
5. Puddle bar .....	0.143 } 0.131 }	0.1465
4. Armour plate ....	—	0.1426
5. Steel.....	0.28 (Eggertz)	0.2972

Several trials were made to burn the iron directly with oxide, without previous decomposition by copper sulphate, but all failed to give the full amount of carbon.

The author has no objection to offer to the ordinary method of combustion with copper oxide in a current of oxygen, but he prefers the use of the Sprengel pump, inasmuch as by its use combustions may be made with greater facility.

J. W.

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**Estimation of Manganese in Cast Iron, Steel, and Bar-iron.**

By F. KESSLER (Deut. Chem. Ges. Ber., v, 605).

THE method of precipitating the iron by means of sodium acetate, and estimating the manganese in the filtrate after separation of all iron by boiling, is the more defective the greater the quantity of sodium acetate added. Direct experiments gave the following numbers, 300 c.c. of liquid being used, and 15 grams of sodium acetate, without any free acetic acid:—

Actual percentage of manganese present	1.00	3.00	7.00	13.00
Loss of manganese in per cent.....	0.21	0.60	0.87	1.06

If, however, the iron solution be treated as follows, 1 gram of sodium acetate is sufficient to precipitate perfectly 1.1 gram of iron from 500 c.c. of liquid, and the precipitate carries down only from 0.02 to 0.05 per cent. of manganese, even from an iron solution containing 13 per cent. of manganese, and in this case the error becomes negligible.

The hydrochloric acid solution of iron chloride is neutralized with sodium carbonate until a permanent precipitate is formed, and then hydrochloric acid is added cautiously until the precipitate is just redissolved; the liquid then contains  $\frac{1}{4}$  of the iron dissolved as hydrate in the iron-chloride solution, this hydrate not being separated by boiling; the acetate is then added, and the whole boiled a few moments.

To avoid washing, the author dilutes the cooled liquid with the precipitate to a known bulk, 500 c.c., and filters off half through a dry filter; the error thus produced is negligible. To estimate the manganese, 10 grams of sodium acetate are dissolved in 150 c.c. of water, 50 c.c. of bromine water are added, and then the manganese solution is added in portions of 50 c.c. each every half hour, another 50 c.c. of bromine-water being added after the third addition of manganese; almost every trace of manganese is thus thrown down as dioxide, and may be estimated by adding hydrochloric acid and a known antimony solution, and then titrating by a standard permanganate solution.

If cobalt is present, a slight error is thus introduced, this metal being thrown down as sesquioxide by the bromine-water. Copper and nickel are precipitated as monoxides.

C. R. A. W.

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**The Determination of Copper and other Metals by Electrolysis.** By the DIRECTORS of the MANSFELD COPPER MINES (Zeitschr. Anal. Chem., xi, 1—16).

DETAILS are given of various improvements that have been made in Leicknow's method for the determination of copper by electrolysis, the extension of this method to the estimation of cobalt and nickel, and of a battery especially adapted for the work. Much depends upon the battery power, which must be varied, according to the richness of the copper ore, and the amount of iron it contains. Considerable advantage was found to accrue by employing a large platinum cone as the negative electrode. The improved process gave accurate results, and

is applicable to the determination of copper in slags, rich copper ores, and furnace-products containing large and small quantities of iron. It is stated that with twelve batteries of three cells, and twelve of six cells, two persons are able to make 10,800 copper determinations in one year.

A. T.

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**Determination of Copper by Potassium Cyanide.** By YVON  
(Compt. rend., lxxiv, 1252).

To avoid the injurious influence of zinc on this reaction, the author proposes the following modification.

Solutions of zinc and copper nitrates, with excess of ammonia containing 1 gram of metal per litre, are first prepared. The amount of cyanide required to decolorise 50 c.c. of pure copper solution is noted, and then the amounts after addition of 5, 10, 15, 20, &c., c.c. of zinc solution. From these results the amounts corresponding to 1 c.c. of cyanide are deduced.

The alloy to be analysed, such as brass, is dissolved in nitric acid, ammonia added, and the whole made up to a litre. After titrating 50 c.c. with cyanide, another 50 c.c. is acidified strongly, boiled with sodium thiosulphate, and the cupric sulphide dissolved in nitric acid and ammonia, and again titrated. The difference represents the zinc.

C. G. S.

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**Quick Method of Separating Copper and Silver.** By R. PALM  
(Dingl. Polyt. J., cciv, 75).

THIS method is based on the fact that silver nitrate is insoluble in concentrated nitric acid, whereas cupric nitrate is soluble. The nitric acid solution of the metals is evaporated to the consistence of a thick oil, and then mixed with concentrated nitric acid free from hydrochloric acid, whereby all the silver salt is precipitated in the crystalline state, the copper salt remaining in solution. The precipitate, which is coloured blue from adhering copper salt, is obtained quite white and free from copper by two or three washings with concentrated nitric acid. The adhering acid evaporates on drying the precipitate. Care must be taken not to evaporate the mixed nitrate solution to dryness, for it is then very difficult to wash out the copper from the precipitated silver nitrate. The more concentrated the nitric acid, the more fully is the silver salt thrown down. An acid of sp. gr. 1.25 is recommended. For every part of concentrated metallic solution, three to four parts of acid are requisite for separation.

W. S.

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**A Method of Estimating Mercury in its Ores.** By A. ESCHKA  
(Dingl. Polyt. J., cciv, 47—50).

THE ore is exposed to a high temperature in contact with metallic iron, and the volatilised mercury is absorbed by metallic gold.



A weighed portion of the pulverised sample is placed in a porcelain crucible, with smooth and even edge, and mixed with about half its weight of pure iron filings, and the whole is uniformly covered with a layer of filings from 0.5 to 1 centim. thick.

The crucible is covered with a concave, well-fitting gold lid, the cavity of the lid being filled with distilled water. The crucible is heated for ten minutes by means of a flame, whose point plays on the under surface. The gold lid is now removed from the crucible, the water poured off, and the mercurial mirror on the convex side is washed with alcohol, the lid dried in the water-bath, and weighed after cooling.

The increase of weight in the gold lid expresses the weight of mercury contained in the sample of ore operated upon.

In the case of rich ores, it is just possible that the amalgam formed on the gold lid may be sufficient in quantity to roll about in a condition of semi-fluidity with the motion of the lid, and on washing with alcohol a little may be removed. When this is the case, the portion of alcohol containing the mercurial globules, must be carefully poured back into the cavity of the lid.

The quantities of various kinds of ore to work upon are as follows:—

The poorest ores containing up to about 1 per cent.	10 grams.
Ores from 1 to 10 per cent. ....	5 „
„ 10 to 30 „ .....	2 „
Ores above 30 per cent. ....	1 „

From tabulated numbers, the results appear to be very accurate.

W. S.

### Purification of Sugar Solutions for the Optical Saccharometer.

By P. CASAMAJOR (Chem. News, xxv, 306).

THE statement of Dr. Stammer, namely, that animal charcoal withdraws sugar from its solutions, and is consequently inapplicable to the purification of saccharine solutions for polarimetric analysis, is objected to by the author as incorrect; and the following experiments are offered in support of the contrary opinion.

A solution of light-coloured sugar, in which the saccharometer indicated 90 per cent., was filtered over animal charcoal containing 3.8 per cent. of water; the saccharometer showed a loss of 2.0 per cent. of sugar. Another portion of the same solution filtered through charcoal containing 8.8 per cent. of water, showed in like manner a loss of 5.0 per cent. of sugar; the reading of the saccharometer being 85.0 per cent. These results show that the presence of water in the bone-black certainly does affect the strength of the solution.

By operating with perfectly dry charcoal, no loss of sugar whatever was indicated by the saccharometer, and although the experiment was several times repeated, no variation in the result was observed.

According to the experiments of Dr. Stammer, the differences between the percentages of sugar are very small, frequently less than

one-half per cent. Such variation is in reality within the limits of experimental error, the indications of the saccharometer being always liable to slight variation, especially with solutions which are not perfectly colourless.

In order to obtain colourless solutions, the author prefers to use, instead of bone-black, a solution of subacetate of lead. The lead solution is added to the solution of sugar in quantity regulated by the amount of colour to be removed, and subsequently precipitated by some salt capable of giving a dense precipitate with a salt of lead. On filtering the liquid it will be found almost, if not entirely colourless. A series of experiments have shown that the addition of an alkaline salt does not in any way affect the saccharometric percentage of the solution.

In the examination of sugars of very low quality, which it is necessary to invert, the use of hydrochloric acid produces such a red colour, that the solution cannot be directly examined with the saccharometer. In such cases the addition of a small quantity of stannous chloride, as recommended by Havemeyer, will be found very effective in preventing its formation; and the solution may, after this addition, be heated several times above 70° C., until no variation is shown by the saccharometer.

J. W.

### Remarks on the Estimation of Sugar by Fehling's Solution.

By L. BRUNNER (*Zeitschr. Anal. Chem.*, xi, 32—34).

THE watery extract of potatoes was found so coloured that the sugar, &c., could not be determined by titration. The cuprous oxide produced was therefore collected on a weighed filter, washed and weighed, then oxidized, and again weighed as copper oxide. More copper oxide was then obtained than corresponded with the cuprous oxide, which was subsequently found to be due to the partial solution of the filter by the alkaline Fehling's solution.

A. T.

### Estimation of Beer Extract. By VICTOR GRIESSMAYER (*Dingl. Polyt. J.*, cciv, 250—252).

STATES that the direct estimation by evaporation of a known weight of the liquid to dryness is vitiated by the evaporation of glycerin. No proof of the truth of this assertion is given.

C. H. G.

### Distinction between Phenol and Creasote. By F. A. FLÜCKIGER (*Pharm. J. Trans.* [3], ii, 1008).

THESE two substances may be distinguished as follows:—

Take <i>a.</i> Solution of ferric chloride about	
1.34 sp. gr.....	1 parts
„ <i>b.</i> Creasote .....	9 „
„ <i>c.</i> Alcohol containing about 85 per cent.	
of absolute alcohol .....	5 „
„ <i>d.</i> Water .....	60 „

Now,  $a + b$  mixed assume no peculiar colour.

$a + b + c$  furnish a green solution.

$a + b + c + d$  form a turbid mixture of a dingy-brownish colour, drops of creasote being separated.

By substituting phenol for creasote, then—

$a + b$  will show a yellowish hue.

$a + b + c$  yield a clear brown liquid.

$a + b + c + d$  display a beautiful permanently blue solution, without separation of carboic acid, or the few drops sinking down may be re-dissolved by shaking.

The blue coloration given by phenol renders it possible to detect that substance in the presence of creasote.

J. B.

**Estimation of Uric Acid.** By H. SCHWANERT (*Deut. Chem. Ges. Ber.*, v, 316).

THE author confirms the results of Salkowski (*Virchow. Archiv.*, iii, 60) and of Veit and Tabelin (*Ann. Chem. Pharm. Suppt.*, ii, 313), viz., that uric acid is not completely precipitated from the solution of its salts by hydrochloric acid, 100 c.c. of the filtrate containing 0.0048 gram of uric acid when the acid is thrown down from solution of sodium urate containing 0.05 per cent. uric acid by 10 per cent. hydrochloric acid. The dissolved uric acid may be estimated by addition of excess of ammonia to the filtrate, and precipitation with silver solution; the precipitate readily decomposes; and hence precipitation as silver-salt cannot be recommended for the estimation of the main portion of the uric acid.

C. R. A. W.

**Separation of the Colouring-matter of Blood by a Solution of Tannin.** By H. STRUVE (*Zeitschr. Anal. Chem.*, xi, 29).

To discover traces of blood in urine, &c., add ammonium or potassium hydrate, then a solution of tannin, and, lastly, acetic acid until the solution is slightly acid. If blood be present, a dark-coloured precipitate will immediately form, which, after treatment with ammonium chloride and glacial acetic acid, will yield splendid crystals of hæmatin.

A. T.

## Technical Chemistry.

**Concentration of Sulphuric Acid.** By R. HASENCLEVER (*Deut. Chem. Ges. Ber.*, v, 502).

As the complaints about the want of durability of the leaden pans employed in the concentration of sulphuric acid have become more frequent since zinc has been used for extracting silver from the lead,



the author tried the action of sulphuric acid, at different temperatures, upon samples of lead of various degrees of purity. His experiments seem to prove that pure and soft lead is more easily attacked by hot sulphuric acid than the ordinary harder and less pure metal. Comparing, then, the different modes of concentrating the acid, the author recommends and describes in detail that of Carrier, who passes steam of three atmospheres pressure through leaden worms lying at the bottom of wooden tubs, lined with lead inside, and filled with acid of the specific gravity 1.5, which, as soon as the specific gravity has risen to 1.7, is transferred into another wooden tank of the same kind. This contains, also, a lead worm, through which, in order to utilise the heat of the concentrated acid, the chamber acid is made to pass on its way into the concentration tub. It is further stated that in cases where even a large amount of impurities in the acid is of no consequence, a combination of Glover's towers with Helbig's and Hasenclever's pyrites furnaces has given satisfactory results. A self-acting syphon arrangement is described which prevents too much sulphuric acid from being drawn off from the platinum still by carelessness.

R. S.

**The Aluminium Chlorides of Commerce.** By ALEXANDER MÜLLER (Deut. Chem. Ges. Ber., v, 519—520).

THE author gives analyses of samples of "chloralum."

(1.) Liquid.	Aluminium chloride .....	16.00
	Calcium chloride .....	1.70
	Alkalis (as sulphates) .....	0.10
	Hydrochloric acid .....	1.20
	Water .....	81.00
		<hr/>
		100.00

(2.) Solid matter, soluble in water 40.70, consisting of—

	Aluminium chloride .....	13.40
	„ sulphate .....	4.10
	Calcium „ .....	9.10
	Sodium „ .....	14.10
		<hr/>
		40.70

Soluble in hydrochloric acid 15.50

Insoluble in „ „ 22.90 consisting of Kaolin .. 13.50  
Silicic acid 9.40

Water .....

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100.00

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22.90

No fluorine or phosphoric acid.

M. M. P. M.

### Separation and Utilisation of the Phosphoric Acid from Iron Ores. By JULIUS JACOBI (Chem. News, xxv, 4).

THE ore, powdered if hard, in small pieces if porous, or calcined if pyritous, is treated with gaseous sulphur dioxide, while water is allowed to fall upon it; or, preferably, a solution of sulphurous acid is poured over it and allowed to stand until all action has ceased. This is then drained off, and the residue washed repeatedly with water. Insoluble basic phosphates are converted into soluble acid phosphates; the sulphur dioxide is driven off by heating; the phosphates partly precipitated; and lime is added. The resulting precipitate contains all the phosphoric acid, and hence is a valuable substance. The purified ore can now be smelted for pig-iron.

M. M. P. M.

### The Chemical Changes in Puddling in Danks' Rotatory Furnace. By G. J. SNELUS (Dingl. Polyt. J., cciv, 216—228).

AN account is first given of the various ores best adapted for fettling or furnace lining, with remarks as to their qualities. It is also shown that a very infusible ore is required for the lower furnace lining, and one that does not easily crumble down. It was found by Danks that a quantity of crushed iron ore, as free as possible from silica, mixed with milk of lime to a mortar, and then dried at a gentle heat, gave a good lower lining for the furnace-bed. Ore for this purpose must contain no chemically combined water, as softening and flying to pieces would take place in such case. The next lining, the "fix," is formed by introducing upon the lower lining pieces of a pure iron ore, such as the iron mountain ore, ilmenite, or titanite ironstone, containing about 40 per cent. iron, and 25 per cent. titanite oxide, "Blue Billy," the residue obtained after extracting the copper from burnt Spanish pyrites, Pottery, Bilboa, Marbella, and Lisbon ores.

*Method of Working.*—It is here stated that the chief advantage of this kind of furnace is that it enables the puddler either to raise or lower his heat rapidly and at pleasure—in short, gives him a complete control over his fire. The melting down of the iron should be done elsewhere, as the furnace is not well adapted for this, and much carbon is consumed. Snelus proposes an arrangement in which the blast furnace is combined with several puddling furnaces, because then all fuel necessary for the melting would be economised. This could not well be done, since the blast-furnace management would then be complicated, and the workman would be confined for his guidance in the process to the puddling of the iron coming straight from the furnace. He is of opinion that in this process of puddling the oxidation of the iron and of the bodies mixed with it only follows *indirectly* by the influence of the oxide of the furnace-lining, whilst with the ordinary puddling furnace this action is ascribed in great part to the influence of the unburnt air in the furnace. This difference, however, seems unlikely, as in all cases unburnt air from the blowing apparatus comes into the furnace and *directly* oxidises. This is illustrated in the sub-

joined analyses of white iron, which lost the greater part of its carbon in melting down, and this could only be effected by the action of the air.

A charge of pig with squeezer or roll cinder appeared necessary. The composition of this cinder varied much from time to time, but an average sample contained Fe 59.5, P 1.04, S 0.20,  $\text{SiO}_2$ , and insoluble 14.4. A small portion of the iron was in the metallic state, viz., about 1.4 per cent. In puddling, about  $6\frac{3}{4}$  cwt. of cinder on the average were charged per ton of puddled bars, much more than would be obtained in the process itself, whereby at the highest 420 lbs. of cinder per ton of puddled bars would be produced, against 785 lbs. used on the average. The object of this addition is to form a covering for the iron, to protect it from too early oxidation. It however effects a slow oxidation itself, and gives up a portion of its iron to the charge. This addition may be dispensed with in the case of white iron, more furnace lining of the best quality being used. After the iron is melted, a jet of water is directed against the lining on the descending side, in order to chill a portion of the cinder and to cause it to be carried under the iron cinder at the same time, as in Parry's steam finery. When grey iron is used, this fining process lasts about ten minutes, during which time the iron loses the greatest part of its silicon by oxidation, the silica passing into the cinder; also the sulphur and phosphorus are in part lost, whilst the graphite quite disappears. Snelus has never observed the known blue flame which rises from the metal bath in the ordinary furnace, and concludes that the carbon by the energetic action of the combined oxygen in the furnace lining is at once converted to carbon dioxide. In puddling white pig, if it contains little silicon, the fining process lasts only a very short time, and the boiling commences in two minutes after melting. In this period very little cinder is formed, showing that the silicon is almost entirely eliminated.

*Iron Analyses.*—Snelus endeavoured to discover a method by which the iron may be separated from the cinder by solution, but was unsuccessful, as very dilute nitric acid dissolved both iron and cinder equally well. Free acid not answering, it was thought probable that solutions of metallic salts, such as copper, zinc, or silver chloride, might serve the purpose. A mechanical method of separation was devised, in which the borings of the pigs or puddled bars were finely ground, and the powder passed through a sieve of 80 meshes to the inch, on which the flat metallic particles remained, whilst the short pulverised cinder particles fell through. The powders so obtained were then tested for the amounts of sulphur and phosphorus they contained. As a check, about 5 lbs. of the iron were melted in a graphite crucible in a Siemens's gas furnace, and the cinder separated from the iron in this way. On comparing analyses of iron and cinder in both cases, the mechanical method was found to be very exact.

After the borings of the puddled bar were powdered in the steel mortar, and sieved, the metallic portion, *a*, and the fused iron in the crucible, *b*, contained as follows:—

	Fe.	Si.	S.	P.
<i>a</i> . . . .	99.54	—	0.29	0.43
<i>b</i> . . . .	—	0.56	—	0.43



The puddled bar therefore contained Fe. 94.69, Si. 0.56, S. 0.26, P. 0.41; the cinder, FeO. 3.12, S. 0.01,  $P_2O_5$ . 0.14,  $SiO_2$ . 0.33,  $TiO_2$ . 0.92.

*Carbon*.—As before stated, Snelus assumes that in Danks' furnace the carbon is directly oxidised to dioxide and not to monoxide, as in the ordinary furnace. In this case 6 parts of carbon would be oxidised to dioxide, 16 parts oxygen of the ferric oxide must be taken up, and  $6\frac{2}{3}$  parts of iron reduced. If, however, which is much more likely, the carbon burns only to monoxide, 1 carbon will reduce only  $3\frac{1}{3}$  iron.

*Sulphur*.—If sulphur is burnt by oxide of iron to dioxide ( $SO_2$ ), ferric oxide being reduced to ferroso-ferric oxide ( $Fe_3O_4$ ), then 1 part of sulphur would give 18 parts of ferroso-ferric oxide. But it is more likely that the greater part of the sulphur passes into the cinder as sulphide of iron, which is easily proved by pouring water over hot puddle cinder.

*Phosphorus*.—If it be assumed that phosphorus reduces oxide of iron to metallic iron,  $P_2O_5$  being formed, then 31 phosphorus = 40 oxygen, or 1 phosphorus would give 3 iron.

*Silicon*.—To show that silicon is oxidised at the expense of ferric oxide, Snelus heated 5 grams of crystallised silicon intimately mixed with 8 grams of Bilboa ore in the gas furnace. The silicon was completely converted into silica and mixed with the reduced iron. By such oxidation 14 silicon = 16 oxygen, or 1 silicon =  $2\frac{2}{5}$  iron reduced by it.

*Manganese* is entirely oxidised, and if this be effected by the ferric oxide, then 1 manganese would reduce as much iron.

W. S.

### Precautions to be taken against the injurious Influence of Mercury on the Workmen in the Manufacture of Mirrors.

By A. MERGET (Dingl. Polyt. J., cciv, 51).

THE workshop in which the overlaying of the mirrors is effected, although roomy and well ventilated, has an atmosphere which, from ground to ceiling, is at all times more or less saturated with the vapour of mercury; moreover, the skin, beards, hair, and every part of the clothing of the workpeople (although they only work four hours per day in this atmosphere) are strongly impregnated with *condensed* mercury, so that they are exposed to the dangerous influence of this metal, even after leaving the workshop.

In order to destroy the possibility of the ill-effects resulting from exposure to mercury vapour, the author proposes to diffuse throughout the atmosphere of the chamber or workshop the vapour of some other volatile substance, which, by combination with the mercury vapour, may produce an inert compound (*i.e.*, inert, in the quantity in which it exists in the room). Boussingault has recommended the use of sulphur, as he found that plants affected greatly by mercury vapour, remained uninjured when this vapour was exposed to the neutralising action of sulphur diffused through the room at ordinary temperatures from flowers of sulphur scattered about. The author experimentally disagrees with these results, both with respect to plants and small animals; in fact with regard to the latter, he concludes that the simultaneous inspiration of sulphur and mercury vapour is more injurious

than beneficial. Another difficulty in the use of sulphur is the large evaporating surface it requires; and chlorine is therefore recommended as the best substitute for it. A very small quantity of chloride of lime is all that need be scattered in a room infected with mercury vapour, the latter disappearing in consequence of its combination with the chlorine to form mercurous chloride (calomel). The mercurous chloride which in small quantities is harmless when absorbed by the system in the process of digestion, might be rather injurious when absorbed as a fine powder in the breathing process; this point has yet to be investigated. It is found that washing with water will not remove the mercury from the different parts of the body impregnated with it, but that water slightly chlorinized will do so readily. Weak chlorine water should certainly be used by the workpeople in mirror factories for cleansing the body. The clothes ought to be changed on leaving the work room, and during the time of rest made sound by exposing to the action of dilute chlorine gas.

W. S.

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#### A New Antimony Blue. (Dingl. Polyt. J., cciv, 160).

THIS new colour, at once very beautiful and durable, is easily prepared by dissolving metallic antimony in aqua regia, filtering the solution through ground glass, and adding it to a dilute solution of potassium ferrocyanide as long as a precipitate falls. This blue is scarcely to be distinguished from ultramarine, and is a valuable acquisition for flower-manufacturers. It cannot be employed in contact with lime. Mixed with chrome or zinc-yellow (zinc chromate) it yields a green little inferior to "Schweinfurt green," and is much less poisonous than the arsenic colour.

W. S.

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#### On Potash or Soft soap, its adulterations, and the disadvantages arising therefrom. By HERMANN VOHL (Dingl. Polyt. J., cciv, 53—71).

SOFT-SOAP is prepared from vegetable and animal fats, which are poor in stearic or margaric acids, and from oils containing more or less stearic acid obtained in the stearin manufacture.

The choice of fatty substance used depends upon the market price, and the time of the year. The maker divides his oils into "warm" or "soft," and "hard" or "cold" oils. There will doubtless be a difference in the quality of a soap according as it *does or does not* contain glycerin. A soft soap prepared directly from vegetable or animal fats, contains a smaller proportion of the fat-acid than a precipitated soap, or one prepared from oleic acid.

Various alterations have been made in the composition of soft-soap; thus, both the fat-acids and the potash have been partially replaced by resin and soda respectively. Experience has shown that an addition of 10 per cent. (or 15 per cent. as maximum) of rosin may be made to the oil which is to be saponified, and produces no ill effect in the soap made. 1.5 to 2 per cent. of soda may also be present, and the soap



still be of excellent quality. Rosin and soda are not therefore considered as adulterations. The additions which many manufacturers make of soluble alkaline silicates (water-glass), starch, and pipe-clay, in order to increase the profit on the article, are certainly to be regarded as adulterations. Some makers use one of the above adulterants, others use more, and frequently all are used together. By this means from 100 pounds of oil, 370 pounds, and even over 400 pounds of soap are often obtained, instead of 240 or thereabouts, which could only be obtained if a good article were made.

Soaps adulterated as above, and to a considerable extent, generally contain much caustic alkali, which acts destructively upon both colour and tissue alike. When adulterated with alkaline silicates, they act injuriously on the cloth, by their causticity, and by the mechanical action of the separated silica. The vegetable textures of linen, hemp and cotton suffer indeed by the mechanical action of the silica, but are little affected by the causticity, whereas woollen and silk stuffs suffer very much from both causes.

Pieces of cotton and linen-cloth washed with a soap containing 1.29 per cent. of silica, rinsed in distilled water, and dried, were found on incineration to contain a notable quantity of silica, from which they were previously quite free. That the fibre of the cloth is injured by the presence of silica in washing and rubbing, was proved by a comparative microscopic examination. Lint prepared from linen which had been washed with siliceous soap, and was used in a hospital for dressing wounds, was found to cause serious inflammation, which did not result when lint was used prepared from cloth quite free from silica.

The presence of free sulphur in soap used for washing woollen stuffs is dangerous, as undoubtedly a destructive effect is produced in the substance of the wool. This is proved by treatment with water, evaporation of the filtered liquid, and heating with soda-lime, when the ammonia reaction is indicated (the nitrogen being derived from the wool).

*Qualitative Examination.*—The first point to be observed is, whether the soap is completely soluble in warm distilled water. If it be found to be so, it is evident that no clay or other insoluble matters have been added in the making. Separation after a time of a green, blue or black precipitate, indicates the presence of certain colouring matters. The clear solution is next decomposed by hydrochloric acid, and it is observed, if decomposition takes place with effervescence, and if the escaping gas be carbonic anhydride, or hydrogen sulphide. If the latter, recourse is had to the sodium nitro-prusside test to determine whether the sulphur was present as alkaline sulphide. The decomposition of the soap solution with acid should be effected in a glass vessel furnished with a stopcock; petroleum spirit is then added, and the mixture well shaken. By this means the fat acid and a portion of the rosin are taken up. Afterwards the acid aqueous liquid is separated by the stopcock, and a drop of iodine solution added, when a violet coloration marks the presence of starch in the soap. The presence of silicates (water-glass), &c., is ascertained by evaporation of the solution and ignition of the residue, of which a portion remaining insoluble on treatment with dilute acid,



indicates the presence of silica. The solution from the fat-acids is treated with basic lead-acetate solution, filtered, and the filtrate precipitated with potassium sulphhydrate in excess, and again filtered. The solution after neutralisation with hydrochloric acid, is evaporated to dryness on the water-bath, and treated with a mixture of ether and spirits of wine. After evaporation of this solvent pure glycerin remains behind.

The solution of fatty acids in petroleum spirit, if it be clear, is now mixed in a tall glass cylinder further with nine or ten times its bulk of pure spirit. If turbidity is produced, then certainly rosin is present. After some time it settles down as a sticky, brown mass to the bottom of the cylinder.

*Quantitative Estimation.*—1. *Water.* A quantity (6 grams) is heated in an air-bath between watch-glasses, closely fitting, and very nearly air-tight, to about 100°. This air-bath is furnished with an aspirator which draws through it a stream of dry air free from carbon dioxide. The temperature is gradually raised to about 120°. The soap remains in the air-bath till the weight is constant.

2. *Fat-acids.*—Ten or 12 grams of soap are dissolved in warm distilled water, and the solution is decomposed with hydrochloric acid in excess. After cooling to 20°, it is well mixed with a quantity of petroleum spirit (about equal in weight to the soap taken) in a glass furnished with a stop-cock.

The layer of spirit is withdrawn by the tap, and the aqueous solution is washed by one or two further agitations with spirit. The petroleum spirit solution is placed in a tared porcelain dish, or beaker glass, and evaporated at about 30°, and finally at about 100°, in an air or water-bath, and the remaining fat-acids are then weighed.

The rosin is estimated by the addition of excess of petroleum spirit to the fat-acid solution, till no further turbidity is produced. The spirit solution after standing some time is decanted from the rosin which has settled down in the bottom of the glass.

3. *Silica.*—Silica may be contained in the soap in two forms, and two methods are therefore necessary for its determination.

That contained as insoluble silica is first determined in about 10 grams of soap taken. The dissolved silica is determined as usual, in the acid solution remaining after removal of the fat-acid spirit solution.

4. *Starch.*—Ten grams of soap are dissolved in 200 to 300 c.c. of distilled water, and weakly acidified with hydrochloric acid. The solution is then gently boiled, water being added to keep up the bulk, till all the starch is converted into grape-sugar, and the solution ceases to give the blue reaction with iodine solution. The solution is then neutralised with chalk or barium carbonate, filtered, and the sugar estimated by Fehling's method with alkaline copper solution.

*Glycerin.*—The qualitative method, already described, is used for this purpose, with the exception that instead of removing the excess of lead by the subsequent addition of potassium sulphhydrate, a current of hydrogen sulphide is employed.

No. 1 is the result of an analysis of a very good sample of potash soap; No. 2 of very much adulterated soap.

	Fat-acids.	Total K <sub>2</sub> O.	Alkali Na <sub>2</sub> O.	Glycerin.	Water.	Silica (soluble),	
No. 1 ....	41.94	10.21	trace	4.62	43.23	—	= 100.
No. 2 ....	5.52	—	10.69	traces	50.40	33.41	= 100.02
							W. S.

**Attar of Roses.** By Dr. R. BAUR (Dingl. Polyt. J., cciv, 253—256).

THE author, having had the opportunity of collecting a quantity of pure oil of roses which was distilled under his own observation, has submitted it to an examination with a view to establishing the relation existing between its two constituents, elaeoptene and stearoptene (rose oil camphor). The latter when pure is a colourless, scentless solid body, which by the action of the weakest oxidising agents, is converted into the odorous fluid elaeoptene; but as the oil is valued in commerce by the ease with which it solidifies, the conversion of the scentless solid into the oil would reduce instead of increasing the selling value of the product.

A quantity of the oil was freed as far as possible from the camphor by exposing it to a low temperature, and then submitting the mass to centrifugal action, repeating this operation on the fluid portion as long as any solid separated from it on exposure to a freezing mixture.

The oil so obtained was added to a strong alcoholic solution of hydrochloric acid, in which lumps of zinc were immersed, and allowed to stand for some days at ordinary temperatures. At the end of that time, some quantity of a crystalline solid had separated, which, after washing with 75 per cent. spirit, presented all the characteristic physical properties of the natural stearoptene. Its melting point is + 33° C.

C. H. G.

**Action of Animal Charcoal in Sugar Making.** By C. SCHEIBLER (Dingl. Polyt. J., cciv, 236—240).

A CAUSTIC criticism, on a paper by Wernekinck with the above title, of which an abstract is given at p. 259 of this volume. Dr. Scheibler shows by direct experiment that charcoal which has been ignited in hydrogen, possesses the same powers of decolorising vegetable solutions and of absorbing lime from sugar-solutions, as when it is ignited and cooled in the ordinary manner, and that consequently the decolorisation is not due to oxidation by condensed oxygen or the lime absorption to carbonic acid. See also note to abstract of original paper.

C. H. G.

**Manufacture of Starch-sugar free from Gum for the Preparation of Spirit Colouring.** By C. KRÖTKE (Dingl. Polyt. J., cciv, 243—249).

STARCH-SUGAR containing dextrin yields a colouring which turns strong spirit cloudy; it is therefore necessary to prepare a purer material for the colouring of rum, &c. The preparation of the starch-sugar is accomplished in the usual manner, by boiling with sulphuric

acid, but the boiling is continued from 5 to 8 hours after the liquid has ceased to show the starch reaction with iodine, or till a portion of the liquid remains clear when mixed with  $\frac{1}{8}$  vol. of 96 per cent. spirit. The mass is then neutralised with chalk, filtered and evaporated in the usual way to 36° B., and then either used at once for the preparation of colouring or allowed to cool and set.

The preparation of the spirit-colouring is carried out by transferring about 100 kilos. of syrup or block sugar prepared as above to a pan furnished with a stirrer and heated by fire. When the sugar boils, 3 kilos. of crystallised soda in small pieces are slowly added, and the heating is continued till drops of the liquid mass let fall into cold water immediately harden, so that they crack like glass between the teeth, and have no flavour of sugar. Water is now added till the liquid has a thickness of 35° B., when it is fit for sale.

C. H. G.

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**Preparation of Sugar-Colours for Beer, &c., from Potato-Starch Sugar.** By CARL KRÖTKE (Dingl. Polyt. J., cciv, 241—243).

A COLOUR much used for beer, wine, and other weak alcoholic liquids; is prepared by putting 5 kilos. of commercial starch-sugar into a suitable iron vessel and melting it with constant stirring to prevent boiling over. The application of heat is continued till the mass begins to burn and give off a pungent vapour, then 100 grms. crushed carbonate of ammonia are added and well stirred in, and gentle heat continued till the mass becomes so stiff that it is difficult to stir, and a small portion removed on a stick and suddenly cooled in water is quite brittle and without the least sweet taste. Two litres of water are then added and the whole stirred and kept boiling till all lumps are dissolved, and the liquor *when hot* marks 34° Baumé. This colour serves for spirit not stronger than 30—50 per cent.

C. H. G.

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**Manufacture of Aniline Colours without Arsenic.** By GIRARD and DE LAIRE (Compt. rend., lxxiv, 1556—1560).

ALL attempts hitherto made to produce aniline red on the manufacturing scale without the use of arsenic, or to dispose economically of the arsenical residues, have proved unsuccessful. The authors therefore, taking into consideration the fact that only a small proportion, not more than one-tenth of the rosaniline manufactured is used for dyeing, the greater part being consumed in the preparation of other aniline-dyes, have turned their attention to the preparation of these latter by other processes.

The process for obtaining "diphenylamine blue" (which is fully described in Watts's Supplement, p. 161), has proved commercially successful. The authors have also obtained, without the use of arsenic, the violet colours usually produced by acting on rosaniline with alcoholic iodides, by oxidizing the secondary monamines, methylaniline,



methyltoluidine, &c. They expect shortly to produce the green in a similar way.

B. J. G.

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**Adulteration of Aniline Colours.** By W. F. GINTL (Dingl. Polyt. J., cciv, 163).

BRONZE powder and crystals of sugar are two adulterants frequently used. Fuchsine is the dye which most frequently suffers adulteration. Bronze powder is easily detected from its insolubility, but the sugar not so readily. The dye known as "diamond fuchsine" the author has found adulterated with sugar so artfully as to defy the perception of persons thoroughly experienced in the use of these colouring matters. When much sugar is present, a moderately experienced nose will detect an unusual odour when the mixture is heated, and on treating a portion with alcohol it will be noticed that some faintly red crystals remain behind, which dissolve but slowly. The method recommended as the best for the estimation of the amount of sugar present in a sample of fuchsine is as follows:—A weighed portion of the dye is dissolved in hot water and the rosaniline is precipitated as picrate by picric acid solution. The clear yellow solution is now precipitated by solution of basic lead acetate, heated to 110°, filtered, and the filtrate submitted to the polarimetric sugar-test. According to this test, one sample of fuchsine was found to contain 15 per cent. of sugar, another 24·2 per cent., and a third 82·13 per cent. In order that the sugar crystals should take the beautiful green lustre of the real crystals of the rosaniline salt, the author believes the sugar must have been placed in a saturated solution of fuchsine, in strong alcohol, and the whole evaporated carefully to dryness.

An easy method for the detection of sugar is as follows:—A portion of the sample of fuchsine is spread out on a white sheet of paper in a light place, and the crystals are closely examined with a lens. The pure crystals of fuchsine are recognised by their acicular form, and by only appearing red (by transmitted light) at the edges. The appearance of more rounded crystals, and possessing a granite or faint amethyst-red tint, is suspicious. Such crystals should be extracted and heated strongly on the point of a spatula, when a smell of burnt sugar is sufficiently characteristic.

W. S.

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**Cause of Explosions of Flour in Flour-Mills** (Dingl. Polygt. J., cciv, 78).

IF flour be dried and heated to 30° in the water-bath it may be used, like Lycopodium-seed, for producing the appearance of lightning in theatres. Ordinary flour will not do this. It is considered probable, then, that the flour when being ground in the mill, in the passage through the stones, may get heated, and if perchance a spark should be produced by the rubbing of the hard stones together, the ignition and explosion of the flour would follow.

The reason why hitherto explosions have so seldom occurred is pro-

bably that the old millers used to moisten the grain, whereas in mills worked by steam this precaution has been neglected.

W. S.

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**Preparation of Transparent Stereoscopic Pictures on Paper.**  
(Dingl. Polyt. J., cciv, 77.)

WELL-SIZED albuminised paper, not too thick, is used for this purpose. It is sensitized as usual, but laid for exposure with the side not made sensitive and not albuminised, on the negative. Printing is effected rather strongly, toning as usual; the tone is judged of by the transparency. If the picture is to be coloured, this is done on the side not albuminised, where the picture is. Water-colours may be used, and the picture-side takes the colours well and makes no spots. This process, discovered by accident, has been employed for ten years with great success for lamp-pictures.

W. S.

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**Miscellanea.**

*Lead Tubes with a Lining of Tin* (Dingl. Polyt. J., cciv, 252).

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*Spencer's Rotatory Puddling Furnace* (Dingl. Polyt. J., cciv, 757).

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*Applications of Infusorial Earth* (Dingl. Polyt. J., cciv, 258).

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*Filtration of River Water* (Dingl. Polyt. J., cciv., 258).

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*Sulphuring of Woollen Stuffs* (Dingl. Polyt. J., cciv, 259).

BASTAERT recommends that the sulphurous acid be prepared in a separate vessel, and applied to the goods in a glass chamber fully exposed to light.

C. H. G.

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*The Cleansing of Silk* (Dingl. Polyt. J., cciv, 259).

THE old method of washing in soap and water.

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*A Cheap and Harmless Hair Dye* (Dingl. Polyt. J., cciv, 260).

AN aqueous decoction of walnut husks mixed with a little alum.

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*Hydrate of Chloral as an Antiseptic* (Dingl. Polyt. J., cciv, 261).

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*Dr. Louvel's Process for the Preservation of Grain by Keeping in Vacuo*  
(Dingl. Polyt. J., cciv, 261).

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## PAPER READ BEFORE THE CHEMICAL SOCIETY.

XXXI.—*Considerations on some Points of the Theoretic Teaching of Chemistry.*

[THE FARADAY LECTURE, delivered before the Chemical Society,  
May 30, 1872.]

By Professor CANNIZZARO.

GENTLEMEN,—

When I received the flattering invitation to appear before you this year, for the purpose of delivering the Faraday Lecture, I found myself in a state of mind, and in circumstances, as unfavourable as possible to the discharge of a duty so onerous as that of speaking before a learned and dignified auditory like the Chemical Society, and, moreover, in a foreign language, to which I am not much accustomed. With regard to new researches, I had no definite result to communicate which appeared worthy of your attention; and I was at the same time on the point of abandoning my laboratory, my books, and my ordinary way of life, and suspending my studies, for the sake of going to Rome to take part in parliamentary business, and devote myself to long and fatiguing labours, with the view of arranging, and obtaining the means of establishing, a new chemical laboratory in the Eternal City.

Nevertheless, your kindness in thinking of me, imposed on me the obligation of accepting your invitation; and I fortunately called to mind a subject which the celebrated French chemist, Dumas, had promised to treat in 1847, and had thought worthy of occupying the attention of a learned body, like the Academy of Sciences at Paris, namely, the form which, under existing circumstances, should be given to the theoretic teaching of chemistry. I perceived at once that this question was one which I could treat with no other assistance than that derived from my memory, and that, even if I did not succeed in treating it exhaustively, it would at least have the advantage of fixing your attention on a question which it is important to resolve, in the period of complete transformation through which our science is at present passing.

I proceed then to lay before you certain considerations on the limits within which the exposition of general theories should be restricted in the teaching of chemistry, and on the form which should be given to that exposition.



Is it desirable, in explaining all that relates to the meaning, use, and value of chemical symbols, formulæ, and equations, to dispense with the atomic and molecular theory as a superfluous and dangerous speculation, and confine ourselves wholly to the empirical laws on which the formulæ are based?

After many trials in the course of my teaching, I have come to the conclusion, that not only is it impossible to eliminate the atomic theory altogether, but, moreover, that in order to arrive at this theory, it is not desirable to follow the long and fatiguing road of induction. On the contrary, it is better to get to it as quickly as possible, by one of those short cuts which the human mind often takes in order to raise itself quickly to a height from which the relations between phenomena can be discerned at a glance. For whether it be due to the intrinsic nature of chemical phenomena and their relations to our ideas, or to the imperfection of the science in its actual state, certain it is that we have not yet succeeded in enunciating the empirical laws of chemical action with that clearness and precision which has been attained in other cases, as for example, in the enunciation of Kepler's laws relating to the movements of the planets. Hence it follows that the so-called laws of definite reciprocal and multiple proportions, of simple and compound equivalents, and of gaseous volumes, when unaided by the atomic and molecular theory, do not penetrate sufficiently into the minds of the majority of students, and do not become fixed there, but remain like floating isolated objects, without any connection between them.

On the other hand, to embrace all these laws in a single glance, and with clear and distinct vision, it is sufficient to regard the phenomena as if each element were in reality made up of homogeneous atoms, having a special and constant weight, and as if the juxtaposition of these atoms gave rise to the molecules, both of simple and of compound bodies, equal numbers of these molecules being always contained in equal volumes of perfect gases, under given conditions of pressure and temperature—that is to say, it is sufficient to comprehend the atomic and molecular theory in the state of development which it has actually attained.

To the different types of mind which are met with in a school of chemistry, this theory affords the clearest, shortest, most exact, and most accessible summary of all that relates to the origin, meaning, value, and use of empirical formulæ and of equations. It ought, therefore, to be introduced into the teaching of chemistry at an early stage, even if we are disposed to regard it merely as a convenient fiction or artifice to aid the mind in seizing the relations between facts.

There is, indeed, nothing surprising in this necessity for a hypothesis to assist us in the comprehension of laws. It often happens that the mind of a person who is learning a new science, has to pass through

all the phases which the science itself has exhibited in its historic evolution. In the teaching of astronomy, for example, we may, to a certain point, follow step by step the ascending road of induction, because that science itself travelled over the same road in its history, Kepler's laws having, indeed, been discovered before they were interpreted and bound together in a single conception by the theory of gravitation.

But with the history of chemistry the case is different. The birth of the atomic theory was not delayed till all the empirical laws of combining proportions had been independently discovered and precisely known; on the contrary, it was this very theory that led to the discovery of the greater number of these laws, assigned the true value to the little that was previously known on the subject, and devised a language by which the laws in question could be expressed. Go back to the time of Dalton, and read in the history of chemistry by Thomas Thomson, the confession by that chemist of the effect produced on his own mind by the explanation of the atomic theory which Dalton gave him in the course of a short conversation:—"I was enchanted," he says, "with the new light which immediately burst upon my mind, and I saw at a glance the immense importance of such a theory."

A similar effect was produced upon Berzelius. He himself relates, in his early memoirs on chemical proportions, that whilst he was engaged in researches on this subject, and was accumulating analysis upon analysis, without being able to deduce from them any new conclusions, he by chance became acquainted with the theory of Dalton. A great light was immediately diffused over the subject of his studies, and he was soon enabled to see, in the results of his experiments, relations which had previously escaped his observation.

Now, then, is not the mind of a person entering upon the study of chemistry, and enquiring into the relations between the quantities in which bodies combine, in a state similar to that of Berzelius when he was commencing his researches on combining proportions, or to that of Thomson when he heard from the mouth of Dalton himself the explanation of the atomic theory? That same light which instantly struck the minds of Dalton's contemporaries, will, without doubt, enlighten the understanding of all who are commencing the study of chemistry.

Berzelius and Thomson thought the atomic theory so self-evident, that the mere enunciation of it was sufficient to enable the mind to grasp all its consequences; they expressed all facts relating to chemical proportions in the language of the atomic theory, and the formulæ which they introduced were merely another form of that language.

Chemists who have adopted this language have not been able to

change its meaning: hence it has resulted that the atomic theory has become more and more interwoven with the very warp of chemical science, and can no longer be separated from it without tearing the whole tissue. Such, indeed, is the idea expressed by Liebig in his letter to the author of the "Life of Dalton." "All our ideas," he says, "are so interwoven with Dalton's theory, that we cannot carry ourselves back to the times in which that theory did not exist."

I might examine the writings of those who have sought to strip chemistry of the Daltonian hypothesis by using the word "equivalent" instead of atom, and I could easily show you, through the veil of this word (equivalent), the ideas of atom and of molecule which are concealed within it, and are the necessary inheritance of the system of formulæ. It often happens that those chemists who wish to evade the difficulty of defining the words atom and molecule, cannot, in treating certain subjects, actually avoid using these words, though they leave their meaning undecided. In thus dealing with the matter, they think to give proof of a discreet reserve by remaining silent upon subjects respecting which they are not sure; "but this reserve," says M. Dumas, in his remarks on affinity, read to the Academy of Sciences, 21st September, 1868, "is not without its inconveniences; for those who are beginning the study of chemistry endeavour to supplement the silence of their teacher on these matters—the only ones on which they can employ their thoughts, so long as they do not work in the laboratory, and are not led to fix their whole attention on the details of experiments and the management of apparatus. It is unnecessary to add that they go wrong, and that one of the chief obstacles to the diffusion of sound ideas upon chemistry, is perhaps due to this ignorance in which the beginner is left, respecting the nature of the force which chemistry calls into play and that of the atoms which it has to consider."

In reference to the art of teaching—an art which is entirely experimental—the opinion of men like Liebig and Dumas, who have had long experience in the business of instruction, has for me a very great value. I do not hesitate to assert that the theory of atoms and molecules ought to play in the teaching of chemistry a part analogous to that of the theory of vibrations in the teaching of optics. The authority of Wollaston is sometimes cited as of one who proposed to disengage, and succeeded in disengaging, the empirical laws of chemical proportions from the Daltonian hypothesis, in his well known synoptic scale of chemical equivalents, inserted in the Philosophical Transactions for 1814. But in this there is an ambiguity. Wollaston was one of those chemists who most highly appreciated the theory of Dalton, and were most affected by its influence. It was this theory, indeed, which guided him in calculating the numbers which he published under the name of equivalents.



These equivalents were nothing more than the *supposed* atomic weights which Wollaston had calculated for a special purpose, taking oxygen as the decimal base; in fact, he himself says so almost in the same words. He could not give a better explanation of the origin and value of these numbers; neither could he altogether emancipate himself from the theory which had suggested them. Why then did he call them-supposed atoms, or equivalents, and not true atomic weights? Did he repudiate the fundamental idea of Dalton's hypothesis? Far from it; he searched for proofs in support of that idea; was desirous of convincing Sir Humphry Davy of its importance and its great probability; and endeavoured to form for himself a geometrical conception of the position of the atoms.

But his exact mind led him to appreciate the criticisms made by Berthollet and Davy, not against the fundamental idea of the atomic theory, but against its mode of application in the then existing state of the science; that is to say, against what was arbitrary in the choice of one rather than another of several equally probable atomic weights.

Moreover, in his memoir above mentioned, he had set himself the essentially practical and limited task of calculating the composition of salts and the quantities which are concerned in double decompositions; and it would therefore have been altogether superfluous for him to enter upon the theoretical discussion of the choice of true atomic weights. These two reasons are, indeed, assigned by Wollaston himself. But he had likewise a third reason, namely, that the supposed atomic weights coincided in the greater number of cases with the quantities which replaced one another in the double decomposition of salts.

These three reasons which induced Wollaston to prefer the name equivalent have, however, lost all their validity through the progress of our science.

1. The notion of molecule introduced into chemistry, and continually more elucidated and developed, and the method of deducing the weights of elementary atoms from a comparison of the composition of molecules, have eliminated, in the greater number of cases, that arbitrary choice between atomic weights which was objected to by Berthollet, Davy, and Wollaston.

2. The actual state of our science no longer allows us to restrict the use of a table of atomic weights to the practical purpose of calculating the composition of salts and their mutual actions; there is, indeed, a much wider field of transformations and of characters to be included in the chemical formulæ and equations of the present day.

3. Whatever name may be given to the numerical value of the symbols, it is no longer possible to make them coincide in all cases with the equivalent weights.

Those who use the word equivalent in the sense which Wollaston

assigned to it, and for the reasons which induced him to employ it, are therefore guilty of a real and absurd anachronism.

In saying this, I have no wish to revive the doubt which was raised in this Society during the discussion on the remarkable paper by Dr. Williamson, to the effect that there have been several different atomic theories. No. The fundamental idea of the atomic theory always has been and still remains the same. The changes introduced into the manner of considering the distribution of the elementary atoms in compounds, and of interpreting the cause of their combination, and the more recent supposition that the molecule of an elementary body may contain several elementary atoms, have not changed, or even touched the fundamental notion of atoms endowed with different weights. On the contrary, the distinction between the idea of molecule and that of atom, and the new criteria for deducing the weights of molecules, have served only to perfect, confirm, and consolidate the theory of Dalton.

The existing theory of molecules and atoms is but the crowning of the edifice whose foundations were laid by the chemist of Manchester (say rather, if you please, the expansion, as, indeed, Sir Benjamin Brodie has said in his Memoir on the Chemical Calculus).

It is this theory thus developed and perfected which should be introduced at an early stage into the teaching of chemistry at the present day.

I hasten now to enter into the heart of my discourse. I have no hesitation in affirming that the solid base, the corner-stone of the modern theory of molecules and atoms, is the theory of Avogadro, Ampère, Kroenig, and Clausius, on the constitution of perfect gases, that is to say, the hypothesis that *these gases, at equal temperatures and pressures, contain in equal volumes equal numbers of molecules, whatever may be their nature and their weight.*

This theory affords the most logical starting-point for explaining the fundamental ideas of molecules and atoms, and demonstrating the existence of the latter.

If any one amongst you, Gentlemen, still retain any doubt respecting the solidity of this foundation, I would invite him, not so much to examine the mathematical demonstrations of the constitution of gases, and the discussion which has been raised in Germany respecting their exactness, as to review the history of chemistry from the time when Gay-Lussac and Dumas introduced the practice of taking account of the weights and volumes of substances in the state of gas, down to our own days.

The following fact will then be observed. At the outset, the facts of chemistry appeared to be at variance with the hypothesis of Avogadro and Ampère, so that this hypothesis was set aside and

soon forgotten; subsequently, however, chemists, by the very connection of their studies and the spontaneous evolution of the science, were brought back unconsciously to this very theory. In fact, having adopted as the unit of volume, that of the fourth part of the molecular weight of oxygen, they perceived, after some years of research, that the greater number of the best established weights of chemical molecules corresponded to four volumes. The memorable experiments of Williamson on etherification, followed soon afterwards by those of Gerhardt on the anhydrides, and later by those of Frankland and of Wurtz on the radicals, and the conclusions deduced from these experiments, removed the most important exceptions to the law of equal volumes of chemical molecules. Nevertheless, Gerhardt was unwilling to accept this law as a constant principle, a molecular verity, believing, indeed, that it was rigorously applicable only to analogous compounds. He thus stopped half way in the application of Avogadro's theory; and this he did for two reasons, one of which was the prejudice in favour of assigning to all metallic oxides and chlorides, constitutions analogous to that of water and of hydrochloric acid; the other, the anomaly exhibited by the vapour-densities of the ammonia-salts, of phosphorus pentachloride, and of sulphuric acid.

Soon, however, by considerations founded on specific heats, isomorphism, and chemical analogies, the prejudice in favour of the similar constitution of all metallic oxides was eliminated, and chemists were led to adopt a system of atomic weights and formulæ of compounds, which agrees with the law of equal numbers of molecules in equal gaseous volumes in all cases to which that law can be applied. On the other hand, as soon as Deville had demonstrated the fact of the decomposition and recomposition of certain substances in the gaseous state, it was perceived that the anomalies in the densities of certain vapours were due to the circumstance that the weights actually determined belonged, not to homogeneous substances, but to mixtures of the products of their total or nearly total dissociation.

Recent experiments have confirmed this forecast, and at the same time physicists, by considering the constitution of gases under a new point of view, have been brought, independently of chemical considerations, to the supposition of equal numbers of molecules in equal volumes of perfect gases, to which Avogadro and Ampère had previously been led by different modes of interpreting physical phenomena.

Who can fail to see in this long and unconscious march of the science, around and towards a fixed point, the decisive proof of the theory of Avogadro and Ampère? A theory to which we have been led by setting out from different and even opposite points—a theory which has enabled us to foresee several facts which experience has confirmed, must be something more than a mere scientific fiction.



It must indeed be either the actual truth, or the image of that truth, seen through media interposed between our intelligence and the reality.

It appears to me, therefore, that the time has come for inverting the order hitherto followed, in the teaching of chemistry, with the view of explaining all that concerns the relations of chemical formulæ to the weights and volumes of gases: that is to say, instead of starting from chemical criteria to determine the weights of molecules, and then demonstrating their proportionality to the densities of gases, I set out from this latter proposition, which is the theory of Avogadro, Ampère, Krönig, and Clausius, demonstrating it by physical considerations. I found on this theory the demonstration of the limits of divisibility of elementary bodies, that is to say, the existence of elementary atoms; I avail myself of opportunities, as they present themselves, for showing that the weights of molecules, and the numbers of atoms contained in them, deduced by application of this theory, are in accordance with the chemical criteria, introduced in great part by Williamson, and admirably summarised by him in his remarkable memoir on the Atomic Theory; and from this agreement I deduce and measure the degrees of confidence to which these criteria are entitled, and the degree of probability which they enable us to attain in the knowledge of molecular weights, in cases where gaseous densities are not available. I pause for a moment on this capital point of my programme.

I have often heard and read that the law of compound equivalents, as enunciated in elementary treatises, affords a demonstration of the existence of chemical molecules and of their different weights.

I am aware that upon this law Berzelius founded his method of determining the weights of compound atoms. I cannot, however, refrain from observing that what is called the law of equivalents, is not a law distinct from that of the atomic weights or proportional numbers of the elements. The assertion that all compounds must contain elements in quantities proportional to these numbers implicitly contains this law. In fact, compounds must contain quantities of the several elements which are integral multiples of the atomic weights; and in reactions between two or more compounds, giving rise to new products, it follows that the quantities of substances which take part in a reaction, and those of the products obtained, must contain all their elements in entire multiples of the atomic weights.

What, indeed, are the compound equivalents of acids, bases and salts deduced from their mutual actions, if not quantities which contain the elements in entire multiple proportions of the atomic weights?

It follows, therefore, that the determination of these quantities can serve only as a verification of the elementary atomic weights, and as a

confirmation of the law that, by means of these numbers and of integral coefficients, the composition of all bodies may be expressed; but this law does not suffice to determine the weights of chemical molecules or even to demonstrate their existence.

In fact, instead of regarding the mass of a compound body as made up of groups or systems of atoms distinct and separated one from the other, one might suppose that there is nothing intermediate between the elementary atoms and a sensible mass of the compound substance, and that the proportions between the numbers of elementary atoms are the necessary consequence of a certain symmetrical distribution of homogeneous particles, required to form a mass which shall exhibit the character of homogeneity when acted upon by physical forces.

I am very far from affirming that this latter supposition is more probable than that of molecules; I merely wish to explain my idea of the insufficiency of the ratios between the weights of compounds which react upon one another, for demonstrating the existence of molecules, and still more, for demonstrating their relative weights. A commencement of proof of the existence of molecules is attained only when, by the study of substitutions, by a multitude of transformations, and even by the proportions of combinations, we arrive at formulæ multiples of those which are the simplest expression of the elementary composition.

But even if arguments of this nature were quite safe from attack, I should still consider that, in the teaching of chemistry, it is not desirable to make them the starting points of the demonstration of molecular weights, from which is to be deduced all that relates to the system of formulæ. In fact, it is not easy to collect for this purpose a sufficient number of substances, the relative molecular weights of which can be demonstrated by transformations intelligible to beginners, and by short and simple reasonings. In a great number of cases, indeed, it is necessary to have recourse to an accumulation of proofs, no one of which would be sufficient of itself, and we do not thus succeed in imparting a full and firm conviction that a contrary interpretation is impossible. It is sufficient indeed to remember that the chemical proofs adduced by Dr. Williamson to demonstrate the relative molecular weights of ether, alcohol, and water were not at first regarded as conclusive. These concordant proofs required, indeed, to be cemented by the theory of Avogadro and Ampère, and then they carried conviction to the minds of all reasonable chemists.

Moreover, it frequently happens, that arguments of this kind used to demonstrate molecular weights by chemical criteria are intimately connected with the idea of a limit of the division of elementary bodies, and even with our reliance on the atomic weights adopted. Sometimes these reasonings are founded on laws of transformation which must be

supposed to have been deduced from a previous comparison of the molecules. If, then, we were obliged to make use of molecular weights for demonstrating the existence of atoms and deducing the laws of transformations, we should, by taking chemical criteria as starting points, often fall into a vicious circle.

Now all these inconveniences are avoided when we start from the theory of the constitution of perfect gases, which is altogether independent of the notion of atoms and of chemical transformation. In this manner alone can all that relates to the molecular and atomic constitution of bodies be deduced from a single principle, which is, indeed, the most natural passage from physics to chemistry. Is it necessary for me here to declare that I do not admit that difference between the physical molecule and the chemical molecule which some persons have wished to introduce? I believe not, after what I have just explained. I need scarcely even remind you that the notion of a molecule, stripped of all the fantastic detail with which it has been encumbered, has acquired great credit amongst men devoted to mathematical and physical studies. This, indeed, has been already said by Mr. Clerk Maxwell and Dr. Tyndall, in better terms and with higher authority than I can pretend to—by the former in his eloquent discourse at the Liverpool Meeting of the British Association, “On the Relations between the Physical and Mathematical Sciences;” and by the latter in his brilliant lecture “On the Scientific Use of the Imagination.”

I now proceed to sketch in broad outlines the order and form in which, in my course of instruction, I explain the theory of molecules and atoms.

I introduce my pupils to the study of chemistry by endeavouring to place them, by means of carefully selected experiments, on the same level with the contemporaries of Lavoisier, and I hasten to teach them how that renowned French chemist continued and crowned the work commenced by Black, by recognising and proclaiming, as the sovereign ruler of our science, the invariability of the weight of matter in chemical changes, or—to speak with greater scientific precision—the invariability of the mass. One cannot indeed avoid remarking that both Black and Lavoisier deduced this principle, unconsciously perhaps, from the study of the physical transformations of bodies, and extended it to chemical transformations. I cannot let slip this opportunity of reminding you of the great progress due to the union of these two sciences, physics and chemistry, in the same minds.

I endeavour to bring out clearly the great influence which was exerted in the development of chemistry by the application of this principle of the conservation of the mass of matter, as soon as Lavoisier had succeeded in introducing it in a definite manner,—and to show



how this principle has illuminated all our ideas of the characterisation and interpretation of the reactions of bodies, both simple and compound; how it has guided us in forming the language of our science, and suggested experimental methods which have enabled us to follow the peregrinations of matter. I think it highly important to explain to beginners, by the simplest arguments, and in the ordinary forms of expression which they use almost spontaneously, the authority of Lavoisier's principle, which indeed is often concealed in those expressions, having become closely bound up with our reason, and having penetrated, as it were, into the marrow of our bones. In this way students are led to form no other idea of matter than that it is ponderable, that is to say, that it includes all which has mass, and to interpret its transformations solely by the union and separation of ponderable things. This conception (which, indeed, is merely the image of the facts themselves, conceived and summarised by our intelligence) is independent of all special ideas about the nature and constitution of matter. We do not say, indeed, whether it is continuous or discontinuous, at rest or in motion; on these topics we neither affirm nor deny anything. This idea should be made clear at an early stage to those who are beginning the study of chemistry. When once their minds have been well impressed with the truth that the fundamental character, the only constant property of matter, is its ponderability, their attention, in the study of chemical reactions, will naturally be directed to the weights of the reacting substances and of the products of the reaction, whatever may be their physical states and their volumes, which they will regard as merely accessory matters.

They must not be turned aside from this direction, which, indeed, is that of the science itself; on the contrary, we must follow and guide them on the road. I therefore direct their attention to the law of definite proportions. In this part of the course, as it is impossible to evade the difficulty that the hearers must take on trust the numerical results of the experiments from which the constant ratios are deduced, we must at least endeavour, by well chosen examples, to give them clear ideas of the methods by which the experimental data have been obtained, and familiarize them with the different forms and expressions of the proportions thence deduced—that is to say, with the manner of comparing the composition of bodies under different possible points of view.

This recommendation may perhaps appear trivial; but who does not know that the law of multiple proportions escaped the observation of Proust, because he had not learnt to choose between the several possible forms of comparing the numerical results of his analyses?

You see, then, that in advancing step by step in the exposition of chemical facts, I quickly transport my students from the time of

Lavoisier to that of Proust, and immediately afterwards to that of Berzelius, at the moment when, by turning his numbers in different directions, he began to perceive some new relation between them.

At this point I give to the minds of my pupils the same impulse that Berzelius received from the knowledge of Dalton's hypothesis.

I explain this hypothesis apart from all accessories, giving dogmatically the table of elementary atomic weights, and introducing the use of symbols and formulæ. The students will be sure to get before their master in the deduction of carollaries from the theory, and to find out of themselves the methods of verifying these carollaries by experiment, if only they have previously been sufficiently accustomed to compare analyses under different points of view, as I have just recommended.

It will also be easy to convince them that the condition that all compounds must contain the elements in the ratios of the atomic weights and their entire multiples, includes implicitly, not only the laws of multiple and reciprocal proportions, but also those of compound proportions or equivalents, as it is at present enunciated in elementary treatises on chemistry.

Nevertheless it will be impossible to prevent the idea of molecules from springing up in the minds of students after the seed of the Daltonian hypothesis has been sown there. But we may, at least, lead them to mistrust compound equivalents as a means of deducing the weights of these molecules. They will not be slow to perceive how much there is of arbitrary assumption in the choice of the molecular weights of compounds, of the number of elementary atoms contained in them, and of the weights attributed to these atoms, when the only experimental data for directing the choice are such as can be found in the ponderable constitution of bodies. There will then be seen to spring up in their minds the same doubts and difficulties that Berthollet, Davy, and Wollaston conceived respecting the application of the atomic theory to chemistry. It will, however, be easy to convince them that these difficulties would be eliminated if means were at hand for verifying the weights of the molecules.

On the other hand, it is impossible to make any progress in the exposition of chemical facts, without meeting with opportunities of demonstrating the simple ratios which exist between the volumes in the gaseous state, of the quantities of substances which take part in a reaction, and of the products thence resulting, and for enunciating the law of Gay-Lussac in its simplest form (leaving out of consideration all that relates to contractions). Dr. Hofmann has rendered valuable aid in the teaching of chemistry by his ingenious forms of apparatus, which enable us to exhibit the measurement of gaseous volumes to a large number of students. On this point, at least, they will no longer be under the necessity of taking results upon trust. The students will

then eagerly seek for an explanation of these simple ratios between the volumes of bodies in the gaseous state. This, then, is the proper moment for explaining or recalling to them the physical theory of the constitution of gaseous bodies, which, on the one hand, gives the explanation of these ratios, and, on the other, fills up the gap in the methods of determining molecular weights, which they will already have recognized in the theory of Dalton. And here I must not omit to remark that the teacher will employ his time well, and to the great advantage of his pupils, whatever may be their degree of instruction in physics, if, in commencing this exposition of the theory, he recapitulates the physical properties of gaseous bodies by broad outlines, as follows:—

What do different bodies in the state of perfect gas possess in common, and in what do they differ?

It need scarcely be observed that in this rapid glance at the general and special physical characters of bodies in the gaseous state, no account is to be taken of small differences; just as, in the first elementary teaching of astronomy, nothing would be said about the deviations from Kepler's laws. For this purpose again, Hofmann's forms of apparatus come to our aid: for by striking the senses, they impress the mind with a clear idea of the identity of behaviour, under varying pressure and temperature, of different substances, as soon as they have approached sufficiently near to the state of perfect gas. Some importance must also be attached to demonstrating how the different nature of substances shows itself in the different limits of the gaseous state, that is to say, in the different limits of compressibility at equal temperatures, and of cooling under equal pressures, also in the different weights of equal volumes, that is to say, in the densities. The teacher should endeavour to make beginners clearly understand that the numbers thus obtained express constant ratios when the substances in question have attained the state of perfect gas, and that then, if the ratio of the weights of two substances is constant, the ratio between their volumes must likewise be constant.

In comparing the weights and volumes of gaseous bodies, students should be early emancipated from the consideration of special conditions of pressure and temperature. On this point I do not quite agree with those who, in teaching, always make use of concrete weights and concrete volumes of gases, under the particular conditions of pressure and temperature which it has been agreed to call normal. In the first place, these normal conditions are never met with in actual experiment; a calculation is required to reduce the observed volumes; and these volumes have to be expressed in the conventional unit before the proportions between them can be ascertained. Why not compare them directly? In striving to remain faithful to the normal conditions, it is necessary in many calculations to resort to fictions which involve us in



long discussions and explanations. To be consistent, one ought, for example, to introduce into the tables the weight of the *absolute volume* of water-vapour at the temperature of  $0^{\circ}$ , and under the pressure of one atmosphere. To me, however, it appears simpler to say that a volume of water-vapour, as soon as it has attained the state of perfect gas, weighs nine times as much as an equal volume of hydrogen under the same conditions, and that the volumes of oxygen and hydrogen which compose water, and that of the water which results from the combination, are to one another as the numbers  $1 : 2 : 2$ , provided that all these volumes are compared under the same conditions of temperature and pressure. Doubtless we must begin with the concrete cases on which the observation is made. But the experimental demonstrations exhibited, and the examples given for showing the course of the calculation, should serve merely as a means of deducing the numbers which express the ratios, and it is these latter with the use of which the student should be familiarised, and to which the further intellectual labour should be devoted.

For the rest, the exposition of the theory of the molecular constitution of gases, which will immediately follow the summary of their physical characters, and will unite them in a single conception, will likewise aid the student in appreciating the values of these relative numbers, will familiarise him with their use, and make him prefer to employ them. In fact, it will not require a long course of reasoning to convince students of chemistry that, in comparing the different volumes of gases, or the different weights of equal volumes, we compare the numbers or the weights of the molecules, and that in these comparisons we recognize, not their concrete numbers or their concrete weights, but the ratio between these numbers and between these weights.

I am aware that among those who frequent our schools of chemistry there are some whose minds are unable to contemplate these abstract relative numbers without the aid of a tangible and materialised representation. To assist such intellects, I prefer resorting to the innocent artifice of giving a certain aliment to the imagination. I say: suppose that by trials analogous to those of Thomson, we had been led to perceive that the weight of a molecule of hydrogen, for example, was the billionth part of a milligram; then all these relative numbers of densities referred to hydrogen would be concrete weights of the molecules, but would at the same time express the ratios between the weights of equal numbers of molecules, that is to say, of equal volumes in the state of gas. I then repeat the same reasoning with a different value of the unit, and by this artifice I succeed in emancipating the minds of the students from the concrete value of the unit, and in leading them to content themselves with the contemplation of the ratios,

and to use with confidence the numbers which express them. This, however, will not interfere with the very useful practice introduced into English schools, of habituating the students to the application of the theories to concrete cases.

In applying the theory of the constitution of gases to the explanation of the ratios between the volumes of hydrogen, chlorine, and hydrochloric acid, and between those of oxygen, hydrogen, and water-vapour, &c., we are led to the very simple conclusion that in the molecule of hydrochloric acid there is a semi-molecule of hydrogen, and a semi-molecule of chlorine, and that in the molecule of water there is a semi-molecule of oxygen, &c.

Students then perceive that the molecules of hydrogen, oxygen, and chlorine, are not the atoms of Dalton, and it must be admitted that a certain degree of confusion then arises in the minds of beginners respecting the ideas of atom and of molecule.

At this point I say to them:—lay aside the atomic hypothesis of Dalton, forget it for a while, and trust only in the molecular weights deduced from the gaseous volumes.

I suppose that they already understand the experimental methods and the calculations required to deduce these latter numbers and refer them to different units. I then continue:—Make a table of the weights of the molecules of a certain number of bodies—it matters not whether simple or compound—in a form similar to that which I now show you, which is the form that I published in 1858 in my “Summary of a Course of Chemical Philosophy.” Instead of taking for your unit the weight of an entire molecule of hydrogen, take rather the half of this weight, that is to say, the quantity of hydrogen contained in the molecule of hydrochloric acid. These numbers are, in fact, nothing but the weights of equal volumes (of one volume) referred to the weight of the volume of hydrogen made = 2.

I take good care, however, not to say that these weights are the weights of two volumes, for I well remember the confusion excited in my own mind, when I was learning chemistry, by the expressions two and four volumes. To put a little order into my ideas at that time, I had to discover that these numbers two and four arose from the mistake of taking as the unit of volume that of the half or quarter of the molecule. I belonged, that is to say, to that class of weak minds which are unable to deal with numbers, unless they have always before them the kind and value of the unit to which these numbers are referred, and I suppose that amongst my pupils there will always be a certain number who resemble me in this respect.

TABLE I.

Names of substances (whether simple or compound).	Weight of a gaseous volume referred to the weight of a volume of hydrogen made = 2, that is to say, weight of the molecules referred to the weight of a semi-molecule of hydrogen taken as unity.	Elementary composition by weight of gaseous volumes referred to the weight of one volume of hydrogen made = 2, that is to say, weights of the elements composing the molecules referred to the weight of a semi-molecule of hydrogen taken as unity.
Hydrogen .....	...	2 hydrogen.
Hydrochloric acid .....	36.5	1 hydrogen + 35.5 chlorine.
Water .....	18	2 hydrogen + 16 oxygen.
Ammonia .....	17	3 hydrogen + 14 nitrogen.
Marsh-gas .....	16	4 hydrogen + 12 carbon.
Ethyl chloride .....	34.5	5 hydrogen + 24 carbon + 35.5 chlorine.
Carbonic oxide .....	28	16 oxygen + 12 carbon.
Carbonic anhydride .....	44	32 oxygen + 12 carbon.
Ordinary oxygen .....	32	32 oxygen.
Ozone .....	48 (?)	48 oxygen (?).
Free chlorine .....	71	71 chlorine.
Phosphorous chloride .....	137.5	106.5 chlorine + 31 phosphorus.
Arsenious chloride .....	181.5	106.5 chlorine + 75 arsenic.
Mercuric chloride .....	271	71 chlorine + 200 mercury.
Free mercury .....	200	200 mercury.
Stannous chloride .....	189	71 chlorine + 118 tin.
Stannic chloride .....	260	142 chlorine + 118 tin.
Silicic chloride .....	170	142 chlorine + 28 silicon.
Nitrous oxide .....	44	16 oxygen + 28 nitrogen.
Nitric oxide .....	30	16 oxygen + 14 nitrogen.
Free nitrogen .....	28	28 nitrogen.
Free phosphorus .....	124	124 phosphorus.
Phosphoretted hydrogen .....	34	31 phosphorus + 3 hydrogen.
Free arsenic .....	300	300 arsenic.
Arsenetted hydrogen .....	78	75 arsenic + 3 hydrogen.
Propyl chloride .....	78.5	36 carbon + 7 hydrogen + 35.5 chlorine.
Benzene .....	78	72 carbon + 6 hydrogen.



Knowing the elementary composition by weight of the compounds indicated in this table, and having acquired the habit of expressing this composition in different forms, students will be able to calculate the composition by weight of the molecules, by dividing the numbers which express the weights of these latter into parts proportional to the numbers which express the ratios of the elements. The numbers thus obtained indicate the weights of the elements in compound molecules.

For simple substances, the weight of the molecule is exactly that of the element. I insist upon this point, that these weights are referred to the same unit as the weights of the molecules, that is to say, to the weight of hydrogen contained in a molecule of hydrochloric acid. You will observe that I do not forget the recommendation which I made just now of recalling frequently to the memory of my hearers the unit of the numbers which they have to compare. Neither do I forget at this point to call in the aid of the imagination, by supposing for a moment that this unit has one or another concrete value (fractions of a milligram), and then, by pointing out the impossibility in the present state of science, of determining the true concrete value of this unit, I eliminate the fiction which I have made, just as the builder of a bridge knocks away the scaffolding as soon as the bridge is able to stand by itself.

The students can then contemplate the relative numbers which, from the experimental point of view, express the elementary composition of gaseous volumes under similar conditions, and from the theoretical point of view the elementary composition of the molecules.

Having thus completed the table of which I now exhibit a specimen, I invite my pupils to compare the composition of different molecules containing the same element, always understanding that it is a matter of indifference whether this list of molecules does or does not comprise that of the element in the free state.

Here are examples :—

TABLE II.—*Examples of Demonstration of the Law of Atoms.*

Names of substances containing hydrogen.	Weights of hydrogen contained in the molecules referred to the weight of a semi-molecule of hydrogen taken as molecular and atomic unit.	Names of substances containing oxygen.	Weights of oxygen contained in the molecules referred to the weight of a semi-molecule of hydrogen.
Hydrochloric acid ..... Water ..... Free hydrogen ..... Ammonia ..... Marsh-gas ..... Ethyl chloride ..... Ethyl hydride ..... Benzene ..... Propyl chloride ..... &c., &c. ....	1 2 2 3 4 5 6 7 $n \times 1$	Water ..... Carbonic oxide ..... Carbonic anhydride ..... Free oxygen ..... Ozone (?) ..... &c., &c. ....	16 = 16 16 = 16 32 = $2 \times 16$ 32 = $2 \times 16$ 48 = $3 \times 16$ (?) $n \times 16$
Atomic weight of hydrogen = 1 = H.		Atom of oxygen = 16 = O.	
Names of substances containing chlorine.	Weights of chlorine contained in the molecules referred to the weight of a semi-molecule of hydrogen.	Names of substances containing carbon.	Weights of carbon contained in the molecules referred to the weight of the semi-molecule of hydrogen.
Hydrochloric acid ..... Epichlorous anhydride ..... Free chlorine ..... Mercuric chloride ..... Phosphorous chloride ..... Arsenious chloride ..... Stannous chloride ..... Stannic chloride ..... Silicic chloride ..... &c., &c. ....	35.5 = 39.9 71 = $2 \times 35.5$ 71 = $2 \times 35.5$ 71 = $2 \times 35.5$ 106.5 = $3 \times 35.5$ 106.5 = $3 \times 35.5$ 71 = $2 \times 35.5$ 142 = $4 \times 35.5$ 142 = $4 \times 39.5$ $n \times 39.5$	Carbonic oxide ..... Carbonic anhydride ..... Ethyl hydride ..... Propyl hydride ..... Butyric acid ..... Benzene ..... &c., &c. ....	12 = 12 12 = 12 24 = $2 \times 12$ 36 = $3 \times 12$ 48 = $4 \times 12$ 72 = $6 \times 12$ $n \times 12$
Atomic weight of chlorine = 35.5 = Cl.		Atom of carbon = 12 = C.	

The law of atoms then stands out of itself. The weights of each element which enter into the molecules containing it are always entire multiples of one and the same weight; and this minimum quantity, which always enters into the molecules, is called an atom. Here, then, we have the atoms of Dalton, which express not only the weights of the combining elements, which was Dalton's aim, but also the composition of equal gaseous volumes. The molecule of the free element likewise contains its atom a whole number of times: hydrogen, oxygen, and chlorine twice; phosphorus and arsenic four times; mercury and cadmium once.

The atoms of different elements have different weights. This result is not a preconceived hypothesis, but follows directly from the numbers given by experiment. This method removes all doubt as to whether the true atomic weight is a multiple or sub-multiple of that which has been chosen. The comparison of a certain number of bodies of known molecular weight and composition, and containing the same element, is sufficient to show what is the weight of the element which always enters by entire multiples: *this weight is the atom*. It is by no means necessary to compare together all the molecules containing the same elements; neither is it essential to know the molecular weight of the free element; this, indeed, is not known in the case of carbon.

To assign to carbon a particular vapour-density and molecular weight is an arbitrary and utterly useless assumption. We have no doubt that this weight must be an entire multiple of 12, but we have no data from which this multiple can be deduced. I still remember the too protracted infancy of our science, when we were unable to calculate the vapour-densities of organic compounds, without introducing into the calculation the hypothetical vapour-density of carbon.

The notion of elementary atoms distinct from that of molecules; the values of the numbers which express the weights of the former and of the latter; the meaning of the symbols which represent the elementary atoms with their weights, and of the crude formulæ which express the number of atoms contained in the molecules, and the weights of those molecules,—all, indeed, that constitutes the solid skeleton of the fundamental notions of chemical theories,—follows spontaneously and springs up in the mind, clear, sharp, co-ordinated, and connected, when we follow in our exposition of facts and reasonings the order which I have just sketched out. I say, Gentlemen, and I insist upon it, that by this logical process the existence of atoms is deduced as a veritable law. But this law is founded on the hypothesis of the existence of molecules and of their equal number in equal volumes of perfect gases (*cæteris paribus*). Well, now, do you still doubt? Discard, then, this hypothesis after it has served you as an instrument of teaching, and in enunciating the law, talk of equal volumes instead of using the



theoretic name of molecules. The atom will then be the constant quantity of an element which enters by entire multiples into equal volumes of gaseous compounds. Nevertheless, this law,—that is to say, that equal volumes are composed of whole multiples of quantities constant for each element,—will at the same time inevitably call up in the mind the idea of molecule and of atom. But the conceptions of molecule and atom thus arising are deprived of all attributes of form, size, distance, continuity or discontinuity, and the only property inseparably bound up with these conceptions is that of ponderability of the mass, the very definition of matter.

If we have invested the ultimate particles of matter with properties other than ponderability, and sought to form to ourselves images of them in space, this has not been done to account for that class of phenomena which is directly contemplated by chemistry, but for the sake of interpreting physical phenomena. But the theories of these phenomena are not yet defined with sufficient exactness to enable us to interweave them indissolubly with chemical conceptions. If the notions of molecule and of atom have gained a certain amount of credit in physics, as declared by Maxwell and Tyndall, I cannot, on this day devoted to the memory of Faraday, forget his opposition to the molecular and atomic theory in the physical form in which it was then presented. I cannot forget that Faraday's idea has made its way, that it has undergone, and continues to undergo, evolution, like all things that are destined to live. On the other hand, I am not unaware that those who admit the notion of molecules have modified it to such an extent that Laplace would perhaps no longer recognise it; and they go on constantly and imperceptibly altering and developing it, so that after a few years, they may perhaps find themselves on the same ground with the successors of Faraday. I insist, then, on the utility of disencumbering the molecular and atomic theory in the teaching of chemistry of all that is not essentially contained in it; of all, indeed, that is not directly suggested by the facts on which it is based. In this manner we shall preserve to the theory all the plasticity required to bend and adapt it to the progress and evolution of our physical and mathematical conceptions. If, for example, we some day arrive at a conception of matter totally different from that which is now entertained, we may find in that conception the explanation of what we call atom and molecule, and having once translated these words into the new theory, we shall probably continue to use them, just as we go on using the expressions latent heat, capacity for heat, &c., after having discarded the theory by which they were suggested. And here I may seem to go against the recommendation put forth by M. Dumas in the passage which I have already cited from his memoir of 1868, not to keep silent about the nature of the atoms

considered in chemistry. But on carefully considering this passage, I believe that I agree with him. M. Dumas speaks of the disadvantages of reticence in teaching, on matters respecting which there is a lack of certainty, because the pupils themselves supply that which the master has omitted, and in so doing are very apt to go wrong; but he surely does not recommend us to give as certain, things which are only probable, and as known, that of which we are ignorant. Yes, M. Dumas is right; we must not be silent.

Two inconveniences may indeed arise from this silence; either the imagination will revenge itself for the forced inaction to which we would condemn it, by going to work alone, and freeing itself from the restraints of reason; or it will become paralysed and atrophied for want of regulated exercise.

To avoid these two rocks, which I have just pointed out, I leave the imagination, on the one hand, to play its part, even rousing it to activity, and letting it for a while range over the field of the different hypotheses on the molecular and atomic constitution of matter—hypotheses suggested by the aggregate of the physical and chemical properties of bodies; but I then call in the aid of reason to estimate the different degrees of probability of these hypotheses, and in this way I avoid attaching inseparably to the notions of atom and of molecule, any other attribute than that of ponderability. This suffices to explain the use and value of the chemical symbols and formulæ; but we shall not rest within these limits until we have performed a real work of elimination on the different geometric conceptions of the bodies constructed by the imagination.

It is not till the fundamental notions of atom and molecule have been placed upon a solid basis, and made clear by freeing them from everything that is not essentially contained in them, that we are in a position to attack the difficulties encountered in the applications of these notions to particular cases. The smallest difficulty for beginners is doubtless that of understanding the causes which render the determination of molecular weights by densities only approximate, and the methods of rectifying the weights of atoms and molecules by gravimetric analyses. For whatever career students of chemistry may be destined, it is not right to sow in their minds illusions respecting the value of these numbers deduced from experiment; on the contrary, it is necessary to discuss by well chosen examples the limits of approximation to which it is possible to attain, so that the students may be able to appreciate the degree of exactness with which it is possible to resolve the question of simple proportions between the weights of elementary atoms. But the greatest difficulties are those which arise from our ignorance respecting the vapour-densities of the majority of inorganic compounds. It will not do to evade these difficulties by silence. If in

our course of instruction we are sometimes obliged to use formulæ before we have established them, we ought at least not to finish our exposition without having supplied the deficiency. We must discuss the different cases in which the data relating to vapour-densities are defective, especially those in which we have no doubt about the weights of the elementary atoms, but are ignorant of the vapour-densities of certain compounds; afterwards the more difficult cases of those elements which do not form any compounds whose molecular weights can be determined by their vapour-densities. We must explain and legitimise the different auxiliary criteria (specific heat, isomorphism, chemical analogy) to which we have recourse in these cases, by first trying them on the touchstone of the theory of Avogadro and Clausius, by testing, in fact, the agreement of the results obtained by these auxiliary methods, with those which are deduced from the latter theory, whenever the two methods can be followed simultaneously. In this way we may move away from our starting-point or base of operations without at any time losing sight of it. I believe that we falsify the intellectual education of youth if we give the formulæ of all compounds as though they were endowed with an equal degree of probability.

Why, for example, should not pupils be told that the formulæ of the salts of potassium, sodium, and silver are ultimately based on a certain analogy with the corresponding compounds of the alcohol-radicals? And why should they be left in ignorance of the fact that no serious disturbance would be introduced into the general body of our chemical knowledge if it should be shown that the formulæ of all these salts ought to be doubled, tripled, &c., &c.?

Why should they be led to believe that the formulæ of ferrous carbonate and the salts isomorphous with it are as well established as those of the ethers of the glycols, when, nevertheless, Kekulé has been able to make an attempt at doubling them without shaking the foundations of the molecular and atomic theory?

Why not tell them that we have no precise knowledge of the molecular weights of compounds containing water of crystallisation, and that we are even utterly ignorant as to whether the ultimate particles of these hydrated compounds are of the same order as the molecules of gases.

It is not by concealing the obscurity of these questions that we can throw more light into the minds of our pupils. I believe, on the contrary, that their minds will be much more enlightened by presenting each fact to them, without mystery, for what it is worth, and showing them that all the points of our science do not merit an equal degree of confidence.

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If I have laid so much stress on the necessity of thoroughly explaining the value of the symbols and formulæ, and have so strongly recommended you to discuss the various degrees of confidence which the formulæ deserve, it is not that I think that the theoretic teaching of chemistry should be limited to these objects, but that in my opinion they constitute the introduction, preparation, and base of the study of the transformations of matter, which is the true object of our science.

With regard to the manner of introducing the pupils to this study, and directing them therein, the short time that remains will not permit me to do more than offer to you a few isolated remarks on some important points.

The comparison of the atomic constitution of molecules has led chemists successively to the law of substitution, to the type-theory of Dumas, then to that of Williamson and Gerhardt, and finally to the theory of the different quantivalence of atoms and of their mode of attachment—the so-called theory of atomicity—which embraces and comprehends the preceding theories.

On the one hand, it cannot be doubted that in the phase which chemistry is now passing through, it is impossible to eliminate this theory completely from the teaching of the science, inasmuch as it includes several partial laws, brings out many important relations, and guides us for the most part with tolerable certainty in the co-ordination and even in the prevision of a large number of facts.

But, on the other hand, it must be admitted that there is some difficulty in keeping this theory within reasonable bounds, and that it has sometimes happened that, in aiming at too great simplicity and conciseness, it has been enunciated in such a manner as to sow in the minds of beginners illusions most dangerous to their intellectual education.

To avoid these inconveniences, I would advise all teachers to keep well before their minds the historic genesis and evolution of this doctrine, so as to be able to give an exact account of the phase at which, in the course of its development, it has actually arrived. It is still far from being a complete and well established theory, being in fact in a state of rapid transformation. Doubtless it already embraces a large number of facts, but it does not yet embrace them all. Already we begin to see that it is but a side, a partial representation, of the truth, regarded from a limited point of view, something like the first trial of a broader theory, which shall perhaps embrace that of the quantivalence and linking of atoms, just as this latter has already included the theory of types.

Further, it is important to remember that this theory exhibited so little relation to our conceptions of the nature of matter, that it could not even be foreseen. It is, on the contrary, the result of the slow elaboration and laborious comparison of facts expressed by means of the

atomic and molecular theory. Hence the propriety, on the one hand, of never detaching, in our exposition, each part of this doctrine from the particular group of facts which has suggested it, and on the other, of not exceeding the limits of that which is really suggested by the facts themselves.

Let me explain myself. I hold that it is not consistent with the present condition of our science to hasten, at the very outset of a course of chemistry, to define the quantivalence of atoms as a property inherent in them, in order to be able to deduce therefrom, *a priori*, and as corollaries, so to speak, the different modes of combination of the atoms. It is preferable, in my opinion, to scatter the exposition of the several parts of this doctrine, so as to present each one of them as a deduction drawn from the observation and comparison of a determinate group of facts, until we find an opportunity of uniting the fragments into a whole, not forgetting, however, to mark the gaps which exist in the aggregate thus obtained. I have further said, and I insist upon this point, that we must never go beyond that which the facts suggest. It would, indeed, be very hurtful to students to give them to understand that this theory has been raised to a height which it has not yet actually attained; to lead them, for example, to consider as settled the question of the invariable atomicity of each element, or of the rules relating to the variation of this atomicity. We must not be in haste to generalise, by applying to all bodies the rules which belong to a single group.

It is certain, for example, that we cannot pass altogether in silence the observation that certain elements are bi-, quadri-, and even sex-valent, while others are tri-, and quinquivalent. But we are not justified in thence deducing as a general law, that for any given element, the quantivalence always varies by even numbers; still less can we make this partial rule the groundwork of a theoretical explanation of the variability of atomicity.

Above all we should take care that the pupils do not form to themselves any mechanical or geometrical conception of the cause and effects of the quantivalence of atoms; they must be frequently reminded that chemical facts neither prove nor disprove anything relating to the size, form, continuity, distance, relative disposition, &c., &c., of the atoms.

If we are sometimes obliged to talk of the relative positions of the atoms in the molecules, and even to give graphic representations of these positions, we must hasten to remark that these figures are nothing but artifices of the mind, intended to represent to the sight that which in reality we perceive only through the veil of transformations; but that we do not really know what it is that corresponds to that which we call position, either in space, or in the mutual actions of different portions of matter.

These observations do not, however, imply any blame of the conduct of philosophers who imagine and try various hypotheses, pushing them even to their utmost limits. They do what they ought to do for the elaboration of the science. But investigation is one thing and teaching is another; and the teacher should beware of petrifying the minds of his pupils by doubtful and transient hypotheses.

With the reservations just made it is possible, in the teaching of chemistry, to derive great advantage from the theory of atomicity, and at the same to avoid its disadvantages.

In the study of chemical transformations, attention should be directed not only to the ponderable changes which occur in the composition of the molecules, that is to say, to the peregrinations of that which we call matter, but likewise to the electric and calorific phenomena which accompany these transformations.

For a long time, and especially since the epoch of Lavoisier, it has been perceived that the study of matter cannot be separated from that of thermic changes. But at the present time, the connection between the one and the other mode of manifestation of chemical phenomena becomes day by day more evident.

Just as in studying changes of ponderable composition, we have been guided by the principle or law of the conservation of the mass of matter, so in studying the dynamical phenomena connected with chemical action, we begin to let ourselves be guided, and we shall let ourselves be guided more and more, by the principle or law of the conservation of energy. The two studies will complete and enlighten one another.

The interpretation, by means of the atomic and molecular theory, and the theory of atomicity, of that which passes within the molecules will serve us as a guide for comparing dynamical phenomena and for discovering relations which would otherwise escape us. On the other hand, the study of dynamical phenomena will reveal analogies and differences between chemical actions which would not be brought to light by the ponderable equation alone. By the side of each ponderable equation will be placed a thermic or dynamic equation, and these two equations will perhaps become like the two faces of one and the same reality. These two parallel studies will thus converge towards a single theory which will probably embrace both classes of phenomena in a single conception.

But we are still far from this ideal, and in our teaching we must not go beyond the actual state of the science. We ought, however, to place our students on the road along which science is marching, so that they may at least follow its most recent advances. We must therefore teach them the little that is at present well established with relation to



the phenomena of heat and electricity. Above all, we must seek to fix in their minds the fundamental ideas on the measurement of work, and the manner of referring it to chemical action by expressing the latter in the form of the atomic and molecular theory.

In this part of the course, which at the present day we cannot avoid introducing into the elementary teaching of chemistry, we ought certainly to be aided by the preceding and parallel teaching of physics, itself explained in the form and language of the thermodynamic theory.

You must already have perceived, Gentlemen, from what I have said, that in the choice of the methods and subjects of a course of general chemistry, I have always had present to my mind that we are teaching a science which is eminently progressive, and, moreover, at the time of its most rapid evolution. I have always kept in view the idea that students should leave our schools, not only with a certain amount of fixed and well defined knowledge, but likewise with aptitudes and preparation sufficient to enable them to follow the unceasing progress of the science and its transformations; and this applies equally well to those who intend to pursue chemistry as a profession, and to those who have learnt the elements of the science as an auxiliary to other studies or professions. In short, I have always kept before my mind that the aim of our chemical teaching, for one as well for the other class of students, is not only to enrich their memories with a certain amount of positive knowledge, but likewise to co-operate in their sound intellectual education.

Chemistry is indeed one of the sciences that are best adapted to this purpose, affording, as it does, the best opportunities for exercising all the faculties of the human mind, and regulating its harmonious development. It is unfortunately true that some of our young professors of chemistry do not appear to keep sufficiently in view this high aim of our teaching. Many among them, allowing themselves to be carried away by the desire of being brief and concise, and of rendering the approaches of our science accessible even to the least prepared intellects, explain dogmatically all the laws and theories in a synthetic order, concealing their origin and development, and not distinguishing them in any way according to their degrees of probability, and the greater or lesser amount of confidence which should be accorded to them. Others, on the contrary, evade the difficulty by saying nothing about theories, though they cannot eliminate them completely from the web of the science while they are explaining its details. I know by experience the indelible traces which this vicious mode of teaching leaves upon the minds of youth.

It is for this reason that I have endeavoured, in the present lecture, to

direct your attention to the most effectual means of teaching chemistry, so that it may serve as an instrument of intellectual culture, and that students may be able to follow its ulterior developments, and apply it judiciously to other branches of natural science.

When the attention of the distinguished chemists and professors here assembled is once directed to this matter, I am sure that a light will be diffused over the question which I have had the honour to open, much brighter than that which I have been able to throw upon it; and I have no doubt that young professors will find therein a source of counsel well adapted to direct their first steps in the teaching of chemistry, at a time when the difficulty of that teaching has been very much increased by the incessant transformations of our science, which go on with a rapidity almost too great to follow.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
BRITISH AND FOREIGN JOURNALS.

**Physical Chemistry.**

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**Researches in Actino-Chemistry (First Memoir). On the Distribution of Heat in the Spectrum.** By J. W. DRAPER (Phil. Mag. [4], xliv, 104).

THIS paper contains, as the author says, an experimental attempt to correct the generally received notions regarding the constitution of the spectrum. It is pretty generally held that there exists a heat spectrum in the less refrangible regions, a light spectrum in the intermediate, and a spectrum producing chemical action in the more refrangible regions of the complete spectrum. All the experiments that have been made on the distribution of heat in the spectrum have been made by exposing some thermometric arrangement in the various coloured bands of the prismatic spectrum. This, in Mr. Draper's opinion, has an inherent defect, namely, that the prismatic spectrum is contracted in the less refrangible regions and drawn out or extended in the more refrangible regions. On comparing together the prismatic spectrum and the diffraction or interference spectrum, this is rendered plain, and to exhibit it, Mr. Draper gives a plate in which a prismatic spectrum, obtained with a train of flint glass prisms, is placed side by side with a diffraction spectrum. Considering the region between the fixed lines *D* and *E* as the middle of the spectrum, these lines are made to coincide in both, and the remainders of the diagrams are drawn to correspond with the scale fixed upon. It appears, on comparing the two, that the distance from *D* to *A* in the prismatic is only half that in the diffraction spectrum, while the distance from *E* to *H* in the former is about double that in the latter. It is evident from this consideration that the indications of a thermometer carried from one end to the other of a prismatic spectrum give no idea of the true distribution of heat in a spectrum drawn out according to wave-lengths, such as the diffraction spectrum may be. Many years ago Mr. Draper attempted to determine the distribution of heat in a diffraction spectrum itself, but failed on account of the smallness of the quantity of the heat. The experiments now described are equivalent to such a determination.

In the experiment described in the present paper, only the visible spectrum is used. This is free from the complication due to absorption of rays by the prisms; for if perfectly colourless prisms be employed, they cannot be exerting any elective absorption on any of the light rays.

A general description of the experiment may be given as follows. Using Angström's wave-lengths, the length at the line *A* is 7604, and that at the line  $H_2$  3933 measured in hundred-millionths of a centimeter; the middle point of this spectrum is at 5768. This is a little beyond the line *D* at which the wave-length is 5892.

The idea of Mr. Draper is to unite into one focus all the rays whose wave-lengths lie between 7604 and 5768, and apply a thermometric



arrangement; likewise to concentrate into one focus all the rays whose wave-lengths are between 5768 and 3933, and to apply to this focus the thermometric arrangement.

The following is the nature of the optical arrangement for the experiment. A ray of sunlight reflected from a heliostat passes through a slit 1 mm. wide, and falls upon a prism. The prism has on its front face a black paper screen with a rectangular opening just large enough to allow the light from the slit to pass through it. After refraction, the rays fall on a concave metallic mirror. A concave glass silvered in front was generally employed. It had a focus for parallel rays at a distance of 27.9 cm.

It is obvious that there are in front of the mirror in this arrangement three foci. At the distance 27.9 cm. is one giving a spectrum image of the sun. Further off there is a spectrum image of the slit, in which, if the adjustments are properly made, the Fraunhofer lines may be seen. Still farther off is an image of the rectangular opening of the black paper on the front of the prism. This image arises from the recombination of all the rays, and is consequently white.

At the place where the second image with the Fraunhofer lines is found two screens of white pasteboard are arranged. By properly placing one of these, the more refrangible rays up to any chosen line may be intercepted, and with the other the less refrangible rays may similarly be stopped. At the place of the third focus was placed a thermopile, and the measurements of temperature were made by means of it in the ordinary way.

All the precautions taken during the experiments are fully described in Mr. Draper's paper. The effect of the heat of the prism itself, for instance, was determined. The thermopile was covered with a delicate film of lamp-black from burning camphor. The galvanometer, which was not of the best or newest form, is also described. The following are the results of the experiments.

The heat of the whole visible spectrum was determined by placing the two screens above mentioned in such positions as to cut off all the invisible rays and to allow only the rays between the Fraunhofer lines A and H<sub>2</sub> to fall upon the pile. The results of the heat-measurements are set down so as to call the heat of the whole visible spectrum 100. The visible spectrum is then divided into two parts by means of the screens, and the heat of each is measured. The first extends from A to the sodium line D, or more accurately a little further. The second extends from the line D up to H<sub>2</sub>. Four prisms were used of rock salt, flint-glass, bisulphide of carbon (perfectly colourless), and quartz, so cut as to give but one image.

Here are the results of 82 experiments abridged from tables given by Mr. Draper:—

	Heat of whole visible spectrum.	More refrangible part.	Less refrangible part.
Rock salt prism .....	100	52	48
Flint glass prism.....	100	50½	49½
Bisulphide of carbon prism .	100	50½	49½
Quartz prism .....	100	51	49

The experiments were tried at various times of the year and of the day, but all in clear weather.

It is thus shown that if the visible spectrum be divided up into equal parts according to wave-lengths, the two sides of it have equal heating powers. This is what we should find in the diffraction spectrum if we could examine it thermometrically. Doubtless every equal bundle of rays estimated by wave-lengths would have equal heating powers. The ordinary views as to the distribution of heat with a maximum point found at the less frangible end of the spectrum are true only of the prismatic spectrum examined in the ordinary way.

Looking at these experiments, Mr. Draper desires to press the view (which he considers new\*) that the heat of a ray and the light of a ray are not to be distinguished one from the other. "When a [light] ray falls on an extinguishing surface heat is produced. But that heat did not pre-exist in the ray. It arises from the stoppage of the ether waves, and is a pure instance of the conversion of motion into heat," that is of motion of one kind into motion of another kind.

J. T. B.

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**The Influence of Temperature on the Molecular Rotatory Power of some Polarising Substances.** By C. TUCHSCHMID (Zeitschr. f. Chem. [2], vii, 230).

THE author has definitely proved that the molecular rotatory power of a solution of cane sugar is dependent on the temperature, and has found that the standard solution of cane sugar prepared for Soleil's saccharimeter, and possessing a dextro-rotatory power of  $100^\circ$  as indicated by that instrument, possesses after inversion a lævo-rotatory power of  $44.16035^\circ$  at zero, and that this rotatory power is reduced to the extent of  $0.50578^\circ$  for each rise in temperature of  $1^\circ$ . The numbers of Clerget are  $44^\circ$  for the standard solution after inversion, and  $0.5$  for the decrease consequent on each rise of  $1^\circ$  in the temperature. Formulæ are given for the correction, according to the author's numbers, of the inversion-results obtained with Wild's as well as with Soleil's instrument.

The rotatory power of an alcoholic solution of camphor does not vary between  $10^\circ$  and  $40^\circ$ , but that of a solution of tartaric acid increases rapidly with the temperature until this has reached  $27.8^\circ$ , after which point it increases but slowly.

T. B.

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**New Apparatus for submitting Gases and Vapours to the Electric Discharge.** By ARNOULD THENARD (Compt. rend., lxxv, 118).

It was found that, by increasing the surface of the metallic electrodes, Houzeau's ozonising apparatus could be rendered more effective; but as the metals were attacked by the gases acted upon, the author placed one glass tube filled with mercury within a second one, and this

\* This cannot be admitted for an instant.—J. T. B.

within a third glass tube, also filled with mercury. The gas to be examined was passed through the annular space between the innermost and the exterior tube, each of which served as an electrode by being connected with one end of an induction coil. As the electric discharge was found to convert the glass all along its surface into a fine dust, by which the slow discharge was gradually changed into sparks, the mercury had to be replaced by antimonious chloride, which, like other acid liquids, keeps the surface of the tubes smooth by dissolving the glass dust formed. 300 c.c. of oxygen, under the action of a coil, excited by four large Bunsen's elements, yielded:—

(1.) 9 milligrams of ozone in four minutes, in tubes in which the metal was in direct contact with the gas; after some time the action ceased completely, owing to the disintegration of the glass and the oxidation of the metal.

(2.) 8.5 milligrams in fifteen minutes in the three-tube arrangement when mercury was used, but after forty hours only 5 milligrams were produced in the same time.

(3.) 9.2 milligrams in twelve minutes in the three-tube arrangement when antimonious chloride was used; after fifty hours' action the apparatus yielded still 8.5 milligrams in the same time.

The dissociation of carbonic acid by the new apparatus amounted for 300 c.c. to 11 per cent. in sixteen minutes, 19 per cent. in fifty-six minutes, whilst only 10 per cent is decomposed in tubes where the gas is in direct contact with the metallic electrodes. When one of the mixtures produced by the dissociation is exposed to the spark discharge, the proportion of ozone is reduced to 7 per cent.

R. S.

**Exhibition of Electrical Phenomena by certain Metals when rubbed with Carbon Bisulphide.** By TH. SIDOT (Chem. Centr., 1872, 129; Dingl. Polyt. J., cciv, 326).

IT has been observed by Sidot that certain metals become electrical when rubbed in a glass with carbon bisulphide. Iron, silver, and aluminium yield sparks under these conditions, if rubbed sufficiently hard. 15 to 20 grams of granulated silver, and 30 to 40 grams pure carbon bisulphide were brought into a perfectly dry glass tube, and the latter was sealed up. On warming gently and shaking in the dark, sparks appeared in the fluid, and after vigorously shaking, the tube appeared quite luminous. When cold water was poured on the outside of the tube the luminosity disappeared, but reappeared after renewed shaking.

W. S.

**New Galvanic Element of Economical Construction.** By M. GAIFFE (Compt. rend., lxxv, 120).

THIS couple consists of a vessel in which a lead plate, reaching to the bottom, which is covered with a layer of red lead, and a zinc plate, of only half the length, are immersed in a 10 per cent. solution of ammonium chloride. The advantages of this element are great constancy,



small internal resistance, great cheapness, and easy construction; its electromotive force is about one-third of that of a Bunsen's element.

R. S.

**Researches on the Rate of Cooling of Gases.** By JAMIN and RICHARD. (Compt. rend., lxxv, 105—113).

THE difference in the rate of cooling of a thermometer suspended first in a vessel deprived of air, and then in the same vessel containing air, was ascribed by Dulong and Petit to the cooling power of the air, on the supposition that the radiation through the gas took place exactly in the same way as in a vacuum. The formula given by them is, besides, based upon the assumption that the temperature and the pressure of the gas remain the same, whilst the heat of the thermometer is transmitted to the envelope. The authors, in order to determine the exact part played by the gas in this transference of heat, conceive the interior of the vessel to be divided into two equal concentric parts by a partition impermeable to heat, and the inner part to be raised in temperature, and consequently in pressure. If now the partition were suddenly removed, pressure and temperature would evidently be equalised instantaneously through the whole vessel, and the effect would be the same, if not only two, but an infinite number of partitions had been there, and were suddenly withdrawn. From this it is seen that the propagation of heat *within* a gas is instantaneous, and, accordingly, the same in all gases, so that the difference in the rate of cooling observed in different gases must depend entirely on the greater or lesser rapidity with which the heat passes either from the heated body to the gas or from the gas to the envelope. In order to determine the true effect of the gas it was therefore necessary (1) to examine the laws of cooling of a heated gas within an envelope; (2) to estimate the heat which a heated body communicates to the gas surrounding it. The first object was attained by putting a spherical glass vessel of 32 centimeters' diameter, in communication with one arm of a water manometer, the other arm of which was connected with another glass vessel filled with air. The height of the water indicated the slightest change of pressure in the two vessels, which, besides, were connected by a tube furnished with a stopcock, so that communication could be made or interrupted at pleasure. A coil of platinum wire, suspended in the spherical vessel was made red-hot by a galvanic current, which was interrupted as soon as the manometer indicated that the pressure had become constant. When the coil had assumed the temperature of the surrounding gas, the further decrease of temperature and pressure could, on account of the small mass of the coil, be considered as entirely due to the mutual action between the gas and the envelope, and observations of the pressure were now made at the end of every five seconds. The law, deduced from the numbers obtained and expressing the rate at which the heat of a gas is absorbed by its envelope, was, by most ingenious mathematical methods, proved to be identical with Dulong's law, expressing the rate at which the heat of a thermometer is absorbed by the surrounding gas, and is given in several differential equations—

$$\text{I. } \frac{d h}{\delta x} = \frac{n'}{\alpha^{d'}} H^{c'} h^{d'}. \quad \text{II. } \frac{d h}{\delta x} = n' H^{c'} \delta \theta^{d'}.$$

$$\text{III. } p c \frac{d \delta \theta}{d x} = S K H^{c'} h^{d'}. \quad \text{IV. } - \frac{d h}{\delta x} = K \frac{(1 + \alpha \theta)}{r} H^{c'} \delta \theta^{d'}.$$

in which  $H$  = original pressure;  $h$  = increase of pressure;  $x$  = time;  $\theta$  = temperature of the envelope;  $\delta \theta$  = excess of temperature of the gas above that of the envelope;  $S$  = surface of the envelope;  $\alpha$  = coefficient of expansion of the gas;  $r$  = radius of the vessel;  $K$  and  $\left(\frac{n'}{\alpha^{d'}}\right)$  are factors peculiar to each gas;  $c'$  and  $d'$  are constants, which are the same for all gases. (The exact meaning of the two constants  $p$  and  $c$  is not explicitly stated.) The value of the following constants has been determined:—

	Carbonic acid.	Air.	Hydrogen.	Mean.
$\frac{n}{\alpha^{d'}}$ .....	0.732	1.15	2.695	—
$c'$ .....	0.54	0.54	0.54	0.24
$d'$ .....	1.15	1.13	1.20	1.06
				R. S.

**Thermochemical Researches on Compounds formed by Double Decomposition.** By BERTHELOT and LONGUERIE (Compt. rend., lxxv, 101—104).

IN the following thermal reactions performed in the calorimeter used and previously described by the authors, 100 parts of water or 100 parts of 2 per cent. solution of potassic hydrate were made to act upon 1 part of trichloride, tribromide, pentachloride, and oxychloride of phosphorus. It was found that—

1. 1 equivalent of  $\text{PCl}_3$ , decomposed by water, disengaged 63,600 heat-units.

2. 1 equivalent of  $\text{PCl}_3$ , decomposed by HKO solution, disengaged 132,400 heat-units.

3. 1 equivalent of  $\text{PBr}_3$ , decomposed by water, disengaged 64,100 heat-units.

4. 1 equivalent of  $\text{PBr}_3$ , decomposed by HKO solution, disengaged 130,600 heat-units.

5. 1 equivalent of  $\text{PCl}_5$ , decomposed by water, disengaged 118,900 heat-units.

6. 1 equivalent of  $\text{PCl}_5$ , decomposed by HKO solution, disengaged 220,100 heat-units.

7. 1 equivalent of  $\text{PCl}_3\text{O}$ , decomposed by water, disengaged 74,700 heat-units.

8. 1 equivalent of  $\text{PCl}_3\text{O}$ , decomposed by HKO solution, disengaged 148,700 heat-units.

The difference of the reactions 1 and 2, namely, 68,800, must theoretically be equal to 69,200 the sum of the reactions,  $(3\text{KHO}, 3\text{HCl})$  and  $(2\text{KHO}, \text{PO}_3\text{H}_3)$ , and the fact that these numbers do not differ

much from each other, is an independent proof that the results 1 and 2 are trustworthy. The authors, who have verified their other numbers by the same method, and with the same success, draw the following conclusions:—

1. From the fact that the trichloride and tribromide, when decomposed by water, disengage very nearly the same amount of heat, it appears that the substitution of chlorine for bromine in these compounds produces the same thermal effect as the substitution of chlorine for bromine in hydrobromic acid. A similar relation seems to hold good for the chlorides, bromides, and iodides of acetyl, and the bromides and chlorides of the alkali-metals.

2. The heat produced in the decomposition of the chlorides of phosphorus is very nearly proportional to the number of chlorine-atoms converted into hydric chloride.

3. The conversion of  $\text{PCl}_3$  into  $\text{PCl}_3\text{O}$  seems to produce less heat than that of phosphorous into phosphoric acid.

R. S.

### Compressibility of Liquids under High Pressures. By M. L. CAILLETET (Compt. rend., lxxv, 77).

THE following table contains the co-efficients of compressibility of some liquids, re-determined with the application of extremely high pressures.

	Density.	Temperature.	Compressibility corresponding to one atmosphere.	Total pressure applied. Atmospheres.
Distilled water deprived of air .....	1000	+ 8	0·0004451	705
Carbon disulphide.....	—	+ 8	0·0000980	607
Alcohol .....	0·858	+ 9	0·0000676	174
		+ 9	0·0000701	305
		+11	0·0000727	680
Petroleum .....	0·865	+11	0·0000828	610
Essence of petroleum ....	0·720	+10·5	0·0000981	630
Ether .....	—	+10	0·0001440	630
Sulphurous acid.....	—	—14	0·0003014	606

The above numbers are not corrected for the compression of the glass vessel, for the determination of which under these high pressures no method was known. The capillary tube of the piezometer was gilt inside, so that the height to which the mercury had risen could be seen from the height to which it had dissolved the film of gold.

R. S.

### Influence of Pressure on the Phenomena of Endosmose and Exosmose. By M. BECQUEREL (Compt. rend., lxxv, 50).

THE influence of the pressure resulting as soon as one liquid has, by endosmose, been raised above the level of the other, was studied in tubes allowing of a pressure of 2,500 millimeters of water, or of other liquids, the diaphragm used consisting either of parchment-paper or of



bladder, or of unglazed earthenware. It was found that the quantities of liquid passing into the outer vessel were proportional to the pressures, at least when the liquids had been freed, by boiling, from the air dissolved in them; when this precaution was not taken, a great number of air-bubbles separated from the liquid during its passage through the membrane, and remaining at the outer surface and within the pores, caused the flow of the liquid to be very irregular. The following numbers express the relative amounts of different liquids which, under equal pressures, had filtered through in the time of half an hour:—

Hydrochloric acid .....	0.187
Distilled water .....	0.165
Ammonia.....	0.139
Calcium chloride dissolved at 35° C.....	0.055

When a cylinder filled with sodium sulphate, and having its lower mouth tied over with parchment-paper, is immersed in solution of calcium nitrate, a rather compact, but not very thick deposit of crystals of calcium sulphate is formed inside, but no stalactites, which are observed to grow plentifully on the outside of the diaphragm, when the position of the liquids is reversed. When blood from which the fibrin had been removed, was made to filter through a membrane under the same pressure of 150 millimeters of mercury, which is known to prevail in the arteries, only serum was found to pass into the outer vessel. Pressure being, according to the author, favourable to the passage of salt through the diaphragm, Dutrochet's statement that more salt is transported by exosmose than by endosmose is evidently right, inasmuch as the first is aided by the pressure due to the unequal level of the two liquids.

R. S.

### Specific Gravities of Various Watery Solutions. By BENNO

FRANZ (J. pr. Chem. [2], v, 274—308).

THE author has constructed a number of tables of specific gravities of watery solutions of substances which are commonly used in the arts and manufactures. In these determinations he generally used tared litre flasks, every precaution as to accuracy being adopted; a balance carrying  $1\frac{1}{2}$  kilos., and turning with 2 decigrams was employed.

Tables of specific gravities of the following amongst other salts are given:—

Ferric chloride.

Nickel and cobalt chloride (in the case of these salts the specific gravities are almost identical).

Copper chloride.

Iron and chrome alums,

Iron sulphate.

Potassium nitrate.

Iron

Zinc

Cadmium

Cobalt

Nickel

Copper

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Sodium acetate.

Potassium „

Barium „

Oxalic acid.

Potassium oxalate.

For the tables, which take up a large space, the original paper must be consulted.

M. M. P. M.

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*New Hydrometer for taking the Specific Gravities of Saccharine Liquids at Different Temperatures.* (Dingl. Polyt. J., cciv, 424.)

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*The Freezing of Water.* By M. BOUSSINGAULT (Ann. Chim. Phys. [4], xxvi, 321).

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*Physical Phenomena which accompany the Rupture, by freezing of Water, of Hollow Projectiles of Various Calibres.* By C. MARTINS and G. CHANCEL (Ibid., 548—560).

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*The Electrical Condition of Gas Flame.* By J. TROWBRIDGE (American Journal of Science, [3], iv, 4).

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## Inorganic Chemistry.

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**On Atmospheric Ozone.** By A. HOUZEAU (Ann. Chim. Phys. [4], xxvii, 5—66).

IN this paper the author, after giving a history of the researches upon atmospheric ozone since its discovery by Schönbein, describes the reagent with which his own observations have been made, namely, red litmus-paper impregnated over half its surface with a 1 per cent. neutral solution of potassium iodide.

This paper in contact with ozone assumes a blue colour only in the part impregnated with the iodide, this change of colour being due, not to the liberation of iodine, but to oxidation of the potassium, the alkali thus formed changing the colour of the litmus. In this respect the iodized litmus-paper is preferable to iodized starch-paper (Schönbein's reagent), which turns blue when the iodine is set free, and will therefore exhibit this reaction over its entire surface under the influence of free acids, especially nitrous acid, as well as of ozone. The part of the litmus paper which is not iodized serves to reveal the accidental presence in the air of alkaline vapours (free ammonia, ammonium carbonate, &c.) which turn the red litmus-paper blue throughout its whole length; it is impossible, therefore, to mistake the indications. Moreover, the iodized litmus-paper cannot be turned blue by chlorine, bromine, &c., since the chloride and bromide of potassium are neutral.

From a large number of observations made with this reagent in various localities and at different times of the year, the following conclusions are drawn:—

1. The air of the country contains an odoriferous and oxidizing

principle which imparts to it a peculiar odour, and the power of blueing iodized red litmus-paper; also of decolorizing blue litmus-paper with-  
out previously reddening it; and of destroying certain bad smells.

2. That this principle is *ozone*.

3. That ozone exists in the air, normally, but that the intensity with which it acts at any given point of the atmosphere is often very variable.

4. That the air of the country contains at most about  $\frac{1}{450,000}$  of its weight, or  $\frac{1}{700,000}$  of its volume of ozone.

5. That the manifestation of ozone by the iodized litmus-papers is much more frequent in the country than in town.

6. That this difference may be due to the greater circulation of air in the fields.

7. That at Rouen, the frequency of the ozone-manifestations varies with the seasons, being greatest in spring, strong in summer, weaker in autumn, and still weaker in winter.

8. That the maximum of ozone manifestation occurs in May and June (16 ozone days per month), and the minimum in December and January (4 ozone days per month).

9. That with respect to the frequency of ozone manifestation, the meteorological year in our climates may be divided into two great seasons; the *very active season* (spring and summer), comprising 78 ozone days, and the *feebly active season* (autumn and winter), including 32.

10. That in general ozone shows itself most frequently on rainy days (48 ozone days in a hundred of rain, to 28 in a hundred of fine weather).

11. That winds, according to their strength, exert the greatest influence on the manifestation of ozone (24 ozone days in 100 when the air was calm or but slightly agitated, and 60 in 100 when the air was greatly disturbed).

12. That at Rouen, the largest number of ozone days occur when the wind is in the west or south-west, the smallest number when it is in the east.

13. That most frequently an exaggerated manifestation of ozone is in intimate relation to the great atmospheric perturbations, known as storms, gales, and hurricanes (*orages, bourrasques, ouragans*).

14. That these great commotions of the atmosphere act at very great distances. Sometimes they momentarily affect the ozone of entire towns and localities, which nevertheless continue to enjoy very fine weather.

15. That atmospheric electricity appears to be the most active cause of the formation of atmospheric ozone.

H. W.

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**Comparison of the Action of Ozone on Sulphate of Indigo and on Arsenious Acid.** By ARN. THENARD and P. THENARD (Compt. rend., lxxv, 458—465).

LIKE potassium permanganate and various other bodies, ozone decolorizes indigo and oxidizes arsenious acid. But when we compare



the action of ozone on these two bodies, we find a marked difference. Let solutions of arsenious acid and sulphate of indigo be prepared in such a way that equal quantities of potassium permanganate, chloride of lime, or any other ordinary oxidating agent shall oxidize equal volumes of each of them; and let these be considered equal. On applying ozonized oxygen to these solutions, it is found that its action on the sulphate of indigo is three times as great as its action on the arsenious acid. Again, it has been already pointed out by one of these authors, that the action of ozone on sulphate of indigo is completed in two marked epochs. Two-thirds of the oxidation takes place almost instantaneously; but for the remainder of the reaction a considerable time is required. The authors of this paper hope, by an investigation of these peculiarities, to throw some light on the nature of ozone.

The solutions employed are first described. Three indigo solutions requiring respectively 1.182, 29.54, and 88.63 milligrams of oxygen for decolorization of 100 c.c. were prepared. The second solution was generally employed. The strengths of the liquids were determined by means of standard solution of potassium permanganate. The arsenious acid solution required for oxidation 95.30 milligrams of oxygen per 100 c.c.

In the first series of experiments, ozonised oxygen having an oxidating power of about 15 milligrams per litre, was employed, its power being estimated by its effect on arsenious acid. In the second series, ozonized oxygen giving 38 milligrams per litre was used. By methodical trials it was determined what part of the action of ozone on sulphate of indigo is immediate and what part is due to slow oxidation. All the precautions adopted during the experiments are described minutely in the original paper. The following is a general description of the method adopted:—

Fifty-four flasks, holding from 354 to 360 c.c. each, were filled with ozonized oxygen and numbered. The ozone in each flask having an even number, was determined by means of arsenious acid; and it was considered that the quantity of ozone per unit-volume in any one of the flasks with an odd number might fairly be taken as the mean of that contained per unit-volume in the two flasks, one on either side of it. Into the flasks having odd numbers the No. 2 sulphate of indigo solution described above was put. The first flask got 25 c.c., and the quantity increased in the successive flasks by 1 c.c. each time. These flasks were then briskly shaken. It was found that the flask to which 31 c.c. of indigo solution had been given was the last in which the colour disappeared immediately, and that the flask which had received 45 c.c. was the last in which the colour had disappeared on the completion of the slow part of the reaction. On calculation, allowance being made for the size of the flask, the space filled up by the solutions added, and so on, the quantity of ozone being estimated by the arsenious acid test as described above, it was found that the immediate action corresponded to a decolorization of 6.20 c.c. of the indigo solution per milligram of ozone, or, as it should rather be stated, in our present ignorance of the real nature of ozone, 6.20 c.c. per milligram of oxidating power as estimated by the arsenious acid. When the action was completed, 9.63 c.c. of the indigo solution per milligram of

oxidating power of the ozonized oxygen had been decolorised. Thus it appears that if 620 represents the immediate action, 963—620 or 343 represents the prolonged part of the reaction.

Experiments were afterwards made with ozonized oxygen having a much higher oxidating power. The results were very nearly the same, the only difference being that the prolonged action was slightly less in comparison with that which took place instantaneously.

It appears then, comparing the action of potassium permanganate upon the solution of sulphate of indigo, and also the action of ozone as estimated by the arsenious acid process, that the—

Action of potassium permanganate being reckoned as. . . . .	1
Total action of ozone is . . . . .	3
Immediate action . . . . .	2
Prolonged action . . . . .	1

The remainder of the paper is taken up with an examination and discussion of the causes of the prolonged action. From the rapidity of the first part of the complete reaction it may be assumed to be due to the ozone itself; while from the slowness of the second part it may be supposed to be due to some secondary body, formed during the first part of the reaction, and which slowly produces its effect.

The next question was as to the nature of this secondary body. At first it appeared probable that, during the reaction with ozone, peroxide of hydrogen is formed, and that this afterwards slowly decolorizes the indigo. This was indicated by the ether and chromic acid test. There were, on examination, some difficulties in the way of accepting this as the explanation of the matter. After careful experiments, however, the authors came to the conclusion that the slow reaction must be due to the formation of this body during the destruction of the ozone.

J. T. B.

### Preparation of Pure Hydrochloric Acid from Impure Fuming Acid. By E. ZETTNOW (Pogg. Ann., cxlvi, 318).

BETTENDORF has shown (*Zeitschr. f. Chem.*, 1869, 492) that stannous chloride completely separates arsenic from hydrochloric acid: hence a pure acid may be obtained from the commercial yellow product (provided this be free from iron) by adding chlorine water until the liquid blues iodide starch-paper (to oxidise sulphurous acid), then adding 50 grams of commercial tin-salt to every 10 or 12 kilograms of acid, leaving the liquid to stand for twenty-four hours at a temperature of 30°—35°, or for three or four days at the ordinary temperature, and finally by distilling after addition of a little sodium chloride.

C. R. A. W.

**Presence of Ammonia in Snow-water.** By A. VOGEL (N. Rept. Pharm., xxi, 329—330).

As considerable discrepancy exists between the results of Boussingault, Filhol, Knop, and Wolf on this subject, the author tested the snow which had fallen at different times during the past winter, for ammonia, and found that fresh-fallen snow at  $-15^{\circ}$ ,  $-16^{\circ}$ , and  $-19^{\circ}$  in November and December, did not contain a trace of ammonia. If, however, the snow were allowed to melt by standing in an uncovered porcelain basin for twenty-four hours, it contained ammonia which had thus been absorbed from the air. At higher temperatures the snow contained more or less ammonia, somewhat more at  $0^{\circ}$  than at  $-3^{\circ}$ , so that the temperature would seem to have considerable influence on the amount of ammonia present. The place in which the snow is collected naturally affects the result.

C. E. G.

**Thermic Researches on Sulphur.** By BERTHELOT (Ann. Chim. Phys. [4], xxvi, 462—470).

THE author has confirmed Lallemand's observation, that a solution of sulphur in carbon disulphide gives rise, on exposure to the sun's rays, to insoluble sulphur, and he finds that the same effect may be produced by the light of the voltaic arc or that of burning magnesium. He also finds that octohedral sulphur melted below  $130^{\circ}$ , and allowed to solidify during exposure to the solar rays, becomes covered with a pellicle of insoluble sulphur. The formation of insoluble sulphur by the action of light requires the previous solution or fusion of the substance, as solid octohedral sulphur is not changed by the action of the sun's rays.

In order to study the thermic changes involved in the above transformations, it is necessary to know the quantities of heat put in action during the solution of octohedral sulphur; also during its fusion and transformation into the insoluble variety. The heat of solution was found to be  $-12.8$  heat-units for 1 gram, and Person gives  $9.4$  as the latent heat of fluidity. Towards  $113^{\circ}$  insoluble sulphur is changed into ordinary sulphur, sufficient heat being evolved at the same time to soften the mass. This shows that near the melting point the heat disengaged during this transformation of sulphur should be rather less than its latent heat of fluidity. The author also effected the transformation in the cold by contact with solution of hydrogen sulphide, and observed during the action of this reagent an evolution of heat equal to  $2.7$  heat-units per gram of sulphur. The sulphur thus obtained evolves during solution in carbon disulphide  $-15.4$  heat-units per gram, a number about one-fourth greater than that observed during the solution of octohedral sulphur. Hence the author considers it to be a new modification of sulphur, and calls it *soluble amorphous sulphur*. In the course of some weeks it becomes crystalline, and then gives on solution nearly the same number as octohedral sulphur. As the heat evolved during the transformation of insoluble sulphur into the soluble amorphous modification is  $+2.7$  heat-units per gram, and that evolved during the change of soluble amorphous sulphur into the octohedral



variety is  $-2.6$ , the total thermic result of the change of insoluble sulphur into the octohedral modification is, when the change takes place at  $18.5$ , approximately nil. Consequently the heat set at liberty during the above change diminishes from  $112^{\circ}$  to the ordinary temperature.

It will now be seen that during the change of octohedral sulphur dissolved in carbon disulphide into insoluble sulphur, there is an evolution of heat equal to about  $12.8$  heat-units per gram (*i.e.*, the heat of solution), and that the transformation of sulphur, melted at about  $113^{\circ}$ , into the insoluble form, is also accompanied by a disengagement of heat.

T. B.

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**Formation of Metallic Sulphides.** By E. PRIWOZNIK (*Ann. Chem. Pharm.*, clxiv, 46—52).

BRIGHT cadmium, lead, bismuth, antimony, zinc, cobalt, and aluminium are but very slightly acted upon, and only some of them feebly tarnished by several months' immersion in yellow ammonium sulphhydrate.

*Copper* obtained in the galvanoplastic way, immersed in yellow ammonium sulphhydrate to which considerably more sulphur has been added, soon becomes coated with a deposit, which after a while drops off in scales. This is bluish black, and proves to be anhydrous cupric sulphide. This body has hitherto been obtained only of a blue colour in the dry way.

By continuing the digestion in a closed vessel, the copper sulphide loses its blue colour, and becomes brownish black, and the ammonium sulphhydrate becomes perfectly colourless, the former being converted into cuprous sulphide, and the latter into pure ammonium sulphide, containing neither excess of sulphur nor of ammonia. Ammonium sulphide thus obtained was sealed up with bright copper. At first there appeared to be no action, but after some months the copper had become greyish black. Potassium and sodium persulphides behave like the ammonia salt.

A way is here presented of obtaining the pure monosulphides, but unfortunately they sometimes contain traces of copper. A solution of ammonium sulphide thus prepared, and free from copper, was evaporated in a current of hydrogen. The residue was colourless, of alkaline reaction, very deliquescent, soluble in water with considerable evolution of heat, and gave all the reactions of an alkaline monosulphide.

Copper is blackened by sodium thiosulphate, when exposed to its solution for some weeks. At a boiling heat the action of finely divided copper is very rapid, cuprous sulphide and sodium sulphite free from sulphide being the products.

*Silver* immersed in the yellow sulphide becomes covered with a lead-grey adherent crystalline crust of silver sulphide,  $\text{Ag}_2\text{S}$ . Church has found this sulphide encrusting ancient silver vessels buried in the earth. Silver boiled with sodium thiosulphate, becomes coated with silver sulphide.

*Tin* immersed in the yellow sulphide combines with the sulphur to form stannic sulphide, but it does not become coated with it, because of the solubility of the latter in alkaline sulphides.

*Nickel* behaves like tin. It colours the alkaline sulphide, and eventually renders it of a deep black colour. It is thus strikingly distinguished from cobalt.

*Iron* gradually becomes coated with an extremely thin black deposit, easily wiped off.

The above metals behave therefore as they do to the alkaline persulphides at a red heat; they only require more time.

E. D.

**On the Atomicity of Nitrogen, with Examples of the Classification of Nitrogen-Compounds.** By F. SESTINI (*Il nuovo Cimento*, 1871-72, 274-280).

THE author objects to the hypothesis of the variation of equivalence or combining capacity in the same element; and, regarding nitrogen as uniformly quinquivalent, he gives the following formulæ for compounds in which it is generally supposed to be trivalent.

$\text{C}\equiv\text{N}-\text{N}\equiv\text{C}$	Cyanogen.
$\text{C}\equiv\text{N}-\text{NH}_4$	Ammonium cyanide.
$\text{C}\equiv\text{N}-\text{O}-\text{NH}_4$	Ammonium cyanate.
$\text{O}=\text{C}\begin{array}{l} \nearrow \text{NH}_2 \\ \parallel \\ \searrow \text{NH}_2 \end{array}$	Urea.
$\text{O}\begin{array}{l} \nearrow \text{N} \\ \parallel \\ \searrow \text{N} \end{array}$	Nitrogen monoxide.
$\text{O}-\text{N}\equiv\text{N}-\text{O}$	Nitrogen dioxide.
$\text{H}_3\text{N}=\text{NH}_3$	Ammonia.
$\text{O}=\text{C}=\text{C}=\text{O}$	Carbon monoxide.

The formulæ assigned to the last three compounds are twice as great as those determined by the respective vapour densities. This the author attributes to a difference between the physical and the chemical molecules.

H. W.

**On the Constitution of Phosphorus Compounds.** By A. MICHAELIS. Part I. (*Ann. Chem. Pharm.*, clxiv, 9-45.)

THE author first discusses the equivalence or chemical value of phosphorus, which he considers to be quinquivalent. It does not seem to be necessary to give a general abstract of this part of the paper (which extends over 13 pages), because the views of Wichelhaus as to the trivalency of phosphorus have already been controverted by Geuther and the author (*Chem. Soc. J.* [2], ix, 552), and the arguments are not new to chemists.

The author holds that the chemical value of an element must be unchangeable, and that there can be no opposition between this doctrine and that of the existence of weaker affinities in an element and of unsaturated compounds. For the chemical value of an element has

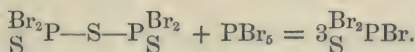
nothing to do with its affinity, which is the force with which the element unites with other elements, and the intensity of which depends upon the nature of all the atoms in a compound. The chemical value of an element is the number of directions in which an atom can exercise its affinity. The affinities of an element may be weaker along some of these lines than along others, for though the lines of attraction of the carbon atom are equal, this appears to be only a particular case of the rule of variable intensities that shows itself in the other elements.

Supposing phosphorus to be only trivalent, the penta-oxygen compounds must be represented as containing a chain of oxygen atoms; but with regard to this linking together of similar atoms, the author points out in refutation of the above supposition, that the atoms of such elements as carbon, which have suggested this linking together, do not do so merely once, twice, or three times, but a number of times limited only by physical causes, whereas we have only  $P_2O_5$  formed in this way—no  $P_2O_6$ ,  $P_2O_7$ , &c.

With regard to the distinction between atomistic and molecular union, which affects the determination of the quantivalence of an element, the author refers to the two criteria by which it has been proposed to distinguish them, namely, the incapability of molecular additions (1) to pass into the state of vapour without decomposition, and (2) to undergo double decomposition. Neither of these holds good when applied; but the author thinks that a modification of the latter when applicable is trustworthy, namely, that when a doubtful compound yields an atomistic compound by double decomposition, it is itself an atomistic one. There can, however, be no uncertainty from this cause as to the quantivalence of any element, if only the whole of its compounds are considered, and not merely particular ones.

*Phosphorus Sulphobromides.* *Pyrophosphoric Sulphobromide*,  $P_2S_3Br_4$  (*Chem. Soc. J.* [2], x, 283).—The author effects the direct combination of bromine with phosphorus trisulphide by adding drop by drop two atoms of the former dissolved in carbon bisulphide, to one atom of distilled phosphorus trisulphide in fine powder, and moistened with carbon bisulphide. The product is entirely soluble in carbon bisulphide, but is separated by ether into an insoluble substance, which appears to be metaphosphoric sulphobromide,  $PS_2Br$  (p. 984), and pyrophosphoric sulphobromide, which dissolves.

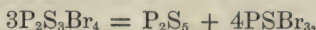
In order further to establish the formula of the pyro-compound, the author treated it with phosphorus pentabromide, and obtained nearly the calculated quantity of orthophosphoric sulphobromide, according to the equation:—



Pyrophosphoric sulphobromide is a liquid of a clear yellow colour, and aromatic, pungent odour, resembling that of orthophosphoric sulphobromide, but still more disagreeable. Its specific gravity is 2.2621 at 17°. It fumes strongly, and becomes turbid when exposed to the air, with separation of sulphur. It cannot be distilled without decomposition; at a higher temperature it decomposes into sulphur, phospho-

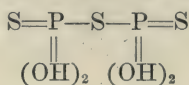


rus pentasulphide, and  $P_2SBr_6$ —a liquid boiling at about  $205^\circ$ . Now orthophosphoric sulphobromide also decomposes into sulphur and  $P_2SBr_6$ ; it may therefore be assumed that the pyro-sulphobromide, in the first place, behaves like pyrophosphoric oxychloride (*Chem. Soc. J.* [2], ix, 1161), and breaks up into  $P_2S_5$  and  $PSBr_3$ , thus:—



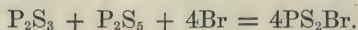
and that then, out of the  $PSBr_3$  the  $P_2SBr_6$  and free sulphur are produced.

The action of water on pyrophosphoric sulphobromide is very complicated, yielding sulphur, orthophosphoric sulphobromide, hydrogen sulphide, phosphorous acid, and a new sulphuretted phosphoric acid, which from its reactions must be a pyrophosphoric acid, probably



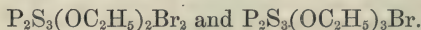
The action of alkalis is like that of water, but more violent, but neither sulphur nor orthophosphoric sulphobromide (which when isolated is unaffected by alkalis) separates out.

The substance, insoluble in ether, which accompanies the pyrophosphoric sulphobromide, yields by analysis numbers approaching those required for *metaphosphoric sulphobromide*; the author indeed believes it to be this body, and attributes its production to the presence of some phosphorus pentasulphide in the trisulphide, explaining its formation by the following reaction:—



Towards water it behaves in an analogous manner to that of the pyro-sulphobromide. With alcohol it forms a very beautiful, crystalline ether,  $P_2S_5O_2(C_2H_5)_4$ , described further on.

*Triethoxypyrophosphoric sulphobromide*,  $P_2S_3(OC_2H_5)_3Br$ .—To prepare this compound, pyrophosphoric sulphobromide is slowly poured into alcohol distilled from sodium. The resulting liquid when poured into water yields a yellow oil consisting of the two ethers,



But on redissolving this in alcohol, allowing the solution to stand for some time, and pouring it again into water, only the triethylated body is obtained. The reason of this is that the substitution of ethoxyl for bromine takes place only with difficulty in presence of much hydrogen bromide.

Triethoxypyrophosphoric sulphobromide is a yellow, transparent liquid having an ethereal odour, recalling, however, that of the sulphobromide. Its specific gravity is 1.3567 at  $19^\circ$ . It cannot be distilled without decomposition, and it fumes slightly in the air after exposure to it for some time. It is slowly decomposed by water and aqueous alkalis, with separation of sulphur. Alcoholic solutions decompose it more quickly, producing mercaptan-like bodies, phosphoric acid, and bromide of the metal.

*Pyrosulphophosphoric ethyl-ether*,  $P_2S_2(OC_2H_5)_4$ .—This is obtained by the further action of alcohol on the last substance. The triethylated bromide is dissolved in three times its volume of alcohol, and the solution kept for some hours at  $40^\circ$ , then after cooling precipitated by water. It is a yellow, faintly aromatic liquid, having an odour somewhat like that of turpentine. Its specific gravity is 1.1892 at  $17^\circ$ . It can be distilled over with steam with only partial decomposition.

Heated to  $60^\circ$  with alcoholic ammonia in a sealed tube, the ether is decomposed, with production of a white, amorphous substance, which must be the amide,  $P_2S_3(NH_2)_4$ .

The author points out, what, however, may be only a coincidence, that the difference of the specific gravities of the pyrobromide and the triethoxylbromide is to that of the pyrobromide and the normal ethyl pyrosulphophosphate as the differences of the quantities of bromine (? ethoxyl) in these compounds are to each other:—

$$\text{Sp. gr. } P_2S_3Br_4 - \text{sp. gr. } P_2S_3(OC_2H_5)_3Br = 0.9054$$

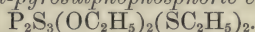
$$\text{Sp. gr. } P_2S_3Br_4 - \text{sp. gr. } P_2S_3(OC_2H_5)_4 = 1.0729$$

$$0.9054 : 1.0729 = 3 : 4$$

$$4 \times 0.9054 = 3.62$$

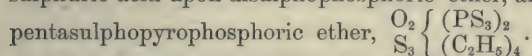
$$3 \times 1.0729 = 3.21$$

*Diethoxyl-diethylsulphyl-pyrosulphophosphoric ether*—

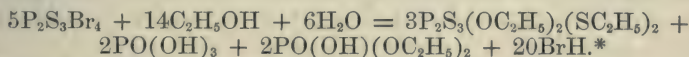


In drying the preceding body over sulphuric acid, this compound is deposited in small white crystals, and can be separated from the liquid ether by filtration through asbestos. In considerably larger quantity it is obtained by allowing aqueous instead of absolute alcohol to act upon the pyrophosphoric sulphobromide at a temperature of  $40^\circ$ . But the best source of all is the impure metasulphobromide, already described, treated with alcohol. At first there appears to be no action, but after some time the mixture gets hot, most of the viscid metabromide disappears, and on cooling this remarkable compound separates out in large crystals.

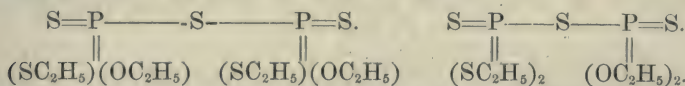
This ether has been already obtained by Carius by the action of sulphuric acid upon disulphophosphoric ether, and described by him as



In the formation of this compound from  $P_2S_3Br_4$ , hydrogen bromide, phosphoric acid, and diethylphosphoric acid are also produced. The last-named body is easily distinguished from ordinary phosphoric acid and monethylphosphoric acid by its soluble lead salt. The reaction takes place thus:—



Theory indicates two isomerides of this ether.



\* This equation is incorrect; the quantities of hydrogen and oxygen on the two sides do not agree.—ED.

The existence of the ethyl derivatives of pyrophosphoric sulphobromide disproves the view that it is a molecular compound, since as the ethyl oxides have free affinities, the  $P_2S_3$  must also have free affinities in order to unite with them.

*Orthophosphoric sulphobromide*,  $PSBr_3$  (*Chem. Soc. J.* [2], ix, 1162; x, 282).—As already mentioned, this compound occurs among the products of the decomposition of the pyrobromide by heat. But it can be conveniently obtained in any quantity by adding 8 parts of bromine drop by drop to the mixed solutions of equal parts of phosphorus and sulphur in carbon bisulphide, evaporating the carbon bisulphide, as far as possible, and then distilling rapidly the muddy looking liquid that remains. Much sulphobromide distils over unchanged, part of which is obtained at once in the solid state; the rest, which is contained in the liquid in the receiver, is obtained by repeatedly washing this liquid with water until it solidifies to a mass of crystals of a compound of the sulphobromide with water. This compound is dissolved in carbon bisulphide and deprived of its water by calcium chloride. On evaporating the solution, the sulphobromide remains as a yellow liquid which solidifies when touched to a striated crystalline mass. The properties and decompositions of this body have already been described in this Journal at the places referred to above. Its specific gravity is 2.85 at  $17^\circ$ . Its melting point is not  $35^\circ$  as formerly stated, but  $38^\circ$ .

The compound,  $P_2SBr_6$ , boiling at  $205^\circ$ , has been already mentioned as occurring, like the preceding, among the products of the decomposition of the pyrobromide by heat. It is also obtained by the slow distillation of the orthobromide. It is a yellow liquid, which, when immersed in a mixture of ice and salt, solidifies to a white mass melting at  $-5^\circ$ . By repeated distillation it is entirely resolved into sulphur and phosphorous bromide. It must, therefore, be regarded as a molecular addition,  $PSBr_3 + PBr_3$ , analogous to Gustavson's  $POCl_3 + BCl_3$  (*Chem. Soc. J.* [2], x, 120).

By repeatedly washing  $P_2SBr_6$  with water, it is converted into a beautiful yellow crystalline mass, having an aromatic odour, which attacks the eyes. Its specific gravity is 2.7937 at  $18^\circ$ . It is the hydrate of orthophosphoric sulphobromide,  $PSBr_3 + H_2O$ , the water having replaced the phosphorus tribromide. It does not at first fume in the air, but after some days it evolves hydrobromic acid, and is gradually decomposed. It melts at  $35^\circ$ , and then breaks up into the pure sulphobromide and water. This substance might be represented as an atomistic compound,  $PBr_3(SH)(OH)$ , but it is not probably such, for solution of it in carbon bisulphide causes the liberation of the water, which is then removable by calcium chloride.

E. D.

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#### Analysis of Devitrified Glass. By H. MESER (*Dingl. Polyt. J.*, cciv, 390).

SOME glass, which by accident had been kept in a state of fusion for many hours, was found, when cold, interspersed with white crystalline nodules.



The composition of the devitrified (A) and of the unchanged amorphous glass (B) is:—

	A.	B.
Silica .....	76.73	77.08
Alumina.....	1.01	2.08
Ferrous oxide .....	0.57	0.22
Lime .....	5.37	5.77
Magnesia .....	0.41	trace
Manganous oxide .....	0.33	0.14
Potassa .....	7.15	1.18
Soda .....	7.77	13.88
Sulphur .....	0.02	0.25
	<hr/> 99.36	<hr/> 100.60

A. T.

**Action of Mercuric Oxide on Iodide of Potassium.** By CARL JEHN (Arch. Pharm. [3], i, 97).

MERCURIC oxide is entirely soluble in solution of iodide of potassium, in consequence of the formation of caustic potash and the double iodide,  $2\text{KI.HgI}_2$ .

W. A. T.

**Thallium Compounds.** By C. RAMMELSBERG (Pogg. Ann., cxlvi, 592—611).

*Thallium dithionate* (hyposulphate)  $\text{Th}_2\text{S}_2\text{O}_6$ , formed by the double decomposition of thallium sulphate and barium dithionate, is obtained in colourless and transparent crystals, which do not contain water.

*Thallium iodate* is obtained by decomposing thallium sulphate with barium hydrate, and neutralising the thallium hydrate with iodic acid. It forms a white precipitate, which can be heated to  $150^\circ$  without decomposition, and is difficultly soluble in nitric acid, especially after drying. Thallium iodate heated with solution of iodic acid, does not dissolve, but is coloured yellow, and on boiling a little free iodine is evolved; this is owing to the formation of *dithallic iodate*, which can also be obtained by heating freshly precipitated thallium trioxide with a solution of iodic acid; a grey brown crystalline salt is then obtained, which is difficultly soluble in nitric acid, and is decomposed by digestion with alcoholic solution of potassium hydrate. On heating, it first turns white, then yellow, melts, and evolves oxygen and iodine, whilst there is a partial sublimation of thallium iodide and oxide. The analysis of this substance gave the formula  $\text{Th}_2\text{I}_6\text{O}_{18} + 3\text{aq.}$ , or  $(\text{Th}_2\text{O}_3 + 3\text{I}_2\text{O}_5) + 3\text{aq.}$ \*

*Thallium periodate* has not been isolated; the precipitate formed either by the addition of thallium hydrate to periodic acid, or by mixing solutions of thallium nitrate and tetrapotassium periodate, seems

\* The author supposes the thallic compounds to contain a double atom of thallium,  $\text{Th} = 408$ ; so that the formula of the trioxide becomes  $\text{ThO}_3$ , and that of dithallic periodate  $\text{Th}_2\text{I}_6\text{O}_{18}$ .

to be a mixture of two substances, the iodate  $\text{TIIO}_3$  and the compound  $\text{TI}_2\text{I}_6\text{O}_{18}$ .

*Dithallium periodate* can be prepared by warming freshly precipitated thallium trioxide with periodic acid. It is a light brown precipitate, and seems to have the composition  $\text{TI}_{20}\text{I}_6\text{O}_{51} + 90\text{aq.}$ , which may be considered as  $\left. \begin{matrix} \text{TI}_2\text{I}_6\text{O}_{24} \\ 9\text{H}_6\text{TI}_2\text{O}_6 \end{matrix} \right\} + 63\text{aq.}$ , or  $\left. \begin{matrix} \text{TI}_{10}\text{I}_6\text{O}_{36} \\ 5\text{H}_6\text{TI}_2\text{O}_6 \end{matrix} \right\} + 75\text{aq.}$

*Thallium sesquichloride*,  $\text{TI}_2\text{Cl}_3$  [or rather  $\text{TI}_4\text{Cl}_6$ ], formed by melting thallous chloride in a stream of chlorine, is obtained in yellow scales. The same compound is formed when the brown oxide is dissolved in hydrochloric acid, and the solution evaporated.

*Potassium dithallium chloride* [or *potassio-thallic chloride*],  $3\text{KCl.TlCl}_3 + 2\text{aq.}$ , obtained by adding potassium chloride to a solution of the brown oxide in hydrochloric acid, forms large transparent crystals, belonging to the quadratic or dimetric system. Almost similar crystals are obtained of the corresponding ammonium salt, by using ammonium chloride in the place of potassium chloride. These salts are not decomposed by boiling with water, but are decomposed by alkalis, with separation of brown oxide of thallium.

A *potassio-thallic bromide* is obtained by first precipitating the bromide of thallium, which is then dissolved by digestion with bromine water, and on the addition of potassium bromide the double salt is formed. It is obtained in slightly yellow crystals, which appear to belong to the regular system: the composition of this body is found to be  $3\text{KBr.2TlBr}_3 + 3\text{aq.}$

*Potassium-dithallium iodide* [*potassio-thallic iodide*] is obtained by digesting thallous iodide ( $\text{THI}$ ) with solution of potassium iodide and free iodine. By evaporation on sulphuric acid, the solution gives dark crystals, which, when powdered, are of an intense dark red colour. The crystals belong to the regular system; on slight heating they lose iodine, and are converted into a mixture of potassium iodide and thallous iodide. This salt has the composition  $3\text{KI.2THI}_3 + 3\text{aq.}$  The thallic oxysalts are usually decomposed by water, with separation of  $\text{TI}_2\text{O}_3$ . The oxide precipitated from the sulphate contains only 1.8 per cent.  $\text{SO}_3$ ; there is, therefore, very little basic salt formed.

The *acetate* is easily obtained in considerable crystals by dissolving freshly precipitated thallic oxide in strong acetic acid. The crystals belong to the rhombic system, and, according to Wilm, have the composition,  $\text{TI}_6\text{C}_4\text{H}_6\text{O}_9$ , which is that of a basic salt.

Thallous nitrate,  $\text{TIINO}_3$ , is isomorphous with the trimetric nitrates of the monatomic metals, such as potassium, ammonium, and silver nitrates.

*Thallous perchlorate*,  $\text{TIClO}_4$ , belongs to the trimetric system, and is isomorphous with potassium perchlorate.

*Tri-thallicous phosphate*, like the corresponding lithium salt, is very insoluble. *Dithallicous phosphate* was obtained by Lang in the anhydrous state, but its crystalline form is unknown; the hydrate  $2\text{HTl}_2\text{PO}_4 + \text{aq.}$ , however, belongs to the trimetric system. This latter salt agrees very closely in form with the salt  $\text{Na}_2\text{HPO}_4 + \text{aq.}$  *Mono-thallicous phosphate*,  $\text{H}_2\text{TIPO}_4$ , and diammonium phosphate and arseniate, are isomorphous, and belong to the monoclinic system. From this it

appears that in the three phosphates,  $R'_3PO_4$ ,  $R'_2HPO_4$ , and  $R'H_2PO_4$  H is isomorphous with R'. The unequal hydration of the sodium salts does not allow this to be seen in this series. Thallium and potassium sulphates are also completely isomorphous, belonging to the rhombic system.

The double sulphates of thallium or potassium, with the metals, magnesium, zinc, nickel, or iron, are isomorphous: they belong to the monoclinic system. Thallium alum is also isomorphous with the ordinary alums.

Normal oxalate and bioxalate of thallium are crystalline, and belong to the monoclinic system; the quadroxalate belongs to the triclinic system, and is isomorphous with the corresponding potassium and ammonium salts.

Acid thallium tartrate is isomorphous with the potassium salt, belonging to the rhombic system.

The double tartrates of thallium and sodium, and of thallium and antimony, are isomorphous with the potassium double salts. The picrate of thallium, and of potassium and ammonium, are, however, not isomorphous.

The thallium and rubidium ferrocyanides are isomorphous, belonging to the triclinic system, and crystallising with two molecules of water.

The few crystalline salts which can be formed from the trioxide are not sufficient to compare with the salts of aluminium, iron, &c. The physical properties of thallium are similar to those of lead, but in chemical properties thallium agrees closely with the alkali-metals.

A. P.

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*On a peculiar state of the Molecules of Tin.* By J. FRITZSCHE (Ann. Chim. Phys. [4], xxvi, 321).

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## Mineralogical Chemistry.

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**Myelin.** By A. FRENZEL (J. pr. Chem. [2], v, 401).

THE lithomarge from Rochlitz in Saxony, known as myelin, has been variously represented by the formulæ  $Al_2O_3.SiO_2$  (Kersten) and  $2Al_2O_3.SiO_2 + H_2O$  (Breithaupt). To ascertain its true composition the author analysed a pure snow-white kidney-shaped specimen carefully freed from adhering ferric oxide. This mineral gave in two analyses the following results:—

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	H <sub>2</sub> O.
a....	43·94	39·40	0·42	17·11 = 100·87
b....	44·19	39·58	0·47	16·57 = 100·81

The pulverised mineral heated to 100° give off 2·56 and 2·30 p. c. hygroscopic water. On deducting this water and the lime, the preceding analyses gave—



	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	H <sub>2</sub> O.
<i>a</i> .....	45·27	40·59	14·55
<i>b</i> .....	45·44	40·69	14·27

leading to the formula  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{H}_2\text{O}$ , which agrees with that of nacrite, kaolin, carnat, and the lithomarge of Schenckenstein near Auerbach, Cainsdorf near Zwickau, and a few other localities. All these minerals give up more or less hygroscopic water at  $100^\circ$ , namely carnat from Rochlitz 1·8, lithomarge from Auerbach 1·2, nacrite from Freiberg 0·8, and kaolin from Seilitz 0·15 p. c.

Myelin appears homogeneous under the microscope, and does not polarise light, in which respects it resembles carnat. Nacrite, on the other hand, crystallises in hexagonal plates; kaolin and lithomarge from the above-mentioned localities are likewise crystalline. The crystalline characters of nacrite, kaolin, and crystalline lithomarge, are not sufficiently well made out to enable us to decide whether those minerals belong to one and the same species. Kenngott proposed to unite nacrite with kaolin; crystalline lithomarge is regarded as a hardened kaolin. On the other hand, the amorphous varieties of lithomarge, namely myelin and carnat are identical, and it would therefore be advisable to discard the name carnat altogether.

Myelin of the same composition as that found by Kersten is said to occur at Zidovar near Temesvar in Hungary.

H. W.

### Heterogenite. By A. FRENZEL (J. pr. Chem. [2], v, 404).

A HYDRATED cobaltoso-cobaltic oxide occurring, together with calcespar and pharmacolite, in the nickel and cobalt veins of the Wolfgang Meesen mine at Schneeberg in Saxony. It is amorphous, and occurs in botryoidal and kidney-shaped masses, having a dense fracture. Lustre faint. Colour blackish to reddish-brown: the ignited powder is coal-black. Streak dark brown, with a fatty lustre. Hardness equal to that of calcespar. Sp. gr. 3·44.

Its blowpipe reactions are as follows:—It gives off water when heated in a tube; heated in the forceps it melts with difficulty on the edges, and colours the flame slightly green; appears slightly magnetic after ignition; exhibits cobalt reaction with glass fluxes. It dissolves easily in hydrochloric acid, giving off chlorine and leaving an insoluble residue; the green solution turns red when heated, and gives with ammonia a small precipitate of ferric oxide.

The quantitative analysis of two specimens gave;

	CoO.	O.	CuO.	Bo <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	H <sub>2</sub> O.	Residue.
<i>a</i> ..	59·03	5·03	0·60	0·35	1·20	1·30	1·60	0·45	14·56	16·00 = 100·12
<i>b</i> ..	39·94	2·81	0·56	0·32	9·80	—	3·60	2·02	12·25	32·20 = 103·50

Most of these constituents are foreign to the mineral, and on deducting them, namely the residue, consisting mainly of silica, which remains on dissolving the mineral in acids, as a skeleton made up of large flocks—also the oxides of iron, copper, bismuth, calcium, and magnesium—there remains for the composition of the heterogenite—

CoO.	O.	H <sub>2</sub> O.	or	CoO.	Co <sub>2</sub> O <sub>3</sub> .	H <sub>2</sub> O.
75·17	6·41	18·54		14·32	67·26	18·54
68·83	5·54	24·13		16·24	58·13	24·13

agreeing nearly with the formula,  $\text{CoO} \cdot 2\text{Co}_2\text{O}_3 + 6\text{H}_2\text{O}$ , which requires 14·61 p. c. CoO, 64·61  $\text{Co}_2\text{O}_3$ , and 20·78 water.

Heterogenite was originally mistaken for asbolan or earthy cobalt—a manganese ore—and in fact it exhibits a distinct trace of manganese when fused with sodium carbonate and nitre. One specimen was found to contain nickel in the proportion of 1 pt. nickel to 20 pts. cobalt.

Heterogenite is a product of the decomposition of smaltine or tin-white cobalt (speiss-kobalt); it is interesting as the first mineral in which the amount of cobalt existing as sesquioxide has been actually determined.

H. W.

**Minerals from Elba.** By ANTONIO D'ACHIARDI (Il nuovo Cimento, 1871-72, 419).

THE vein of tourmaliniferous granite near San Piero in Campo in the island of Elba, celebrated for its crystals of Castor, Pollux, and many other minerals, has lately been found to contain crystallised minerals not hitherto known to occur in the island.

One of these is heulandite, which occurs in groups of transparent pale reddish yellow crystals having the form 110, 101,  $\bar{1}01$ , 010, 001, or 111? 110, 101,  $mOp$ ,  $\bar{1}01$ , 010, 001, and all the characters peculiar to the species, including the elements of which it is composed.

Another mineral found in the same granite forms crystalline nodules like those exhibited by gismondine and sometimes by stilbite, and appears from a preliminary analysis by Bechi, to approach very nearly in composition to stilbite.

A third mineral occurs as a crystalline incrustation, covering the more or less decomposed crystals of red tourmaline. whence it appears to resemble *Cookeite*.

A further examination of all these minerals is promised.

H. W.

**The Nolla Slates in the Canton of the Grisons.** By A. VON PLANTA-REICHENAU (Versuchs-Stationen Organ., xv, 241—251).

THESE dark-coloured, friable, thinly-foliated slates are ground in the stream of the Nolla, fed partly from glaciers, to a fine powder, which is deposited as a black mud near the junction of this river with the Rhine, forming a soil possessing valuable chemical and physical properties.

Analyses of the slates, the soil formed from them, and the mud filtered from suspension in the river, gave the following percentage results on the air-dried substances:—

	Slate.	Mud.	Soil.
Loss on ignition .....	1·28	4·50	10·86
Soluble in hydrochloric acid:—			
Lime .....	·38	1·03	3·30
Magnesia .....	·64	·42	1·41
Potash .....	·08	·22	·24
Soda .....	·48	·19	1·03
Phosphorus pentoxide.....	·06	·05	·44
Ferric oxide and alumina ....	4·99	8·40	7·88

These results show that the mud in the flowing river is an intermediate product. Complete analyses of the slate and soil are given.

E. K.

**Ferro-tungstine, a new Mineral.** By HUGO TAMM (Chem. News, xxvi, 13).

FERRO-TUNGSTINE is a dark, steel-coloured, heavy, crystalline powder, formed of separate and distinct crystals, somewhat resembling crystallised silicon. Sp. gr. 12·5. It is very hard, and is with great difficulty reduced to an amorphous powder. When heated in the air to a temperature of low redness, it slowly oxidises, and is converted into a yellow powder of tungstic acid.

Its percentage composition is—

Metallic tungsten.....	88·05
„ iron .....	5·60
„ manganese.....	0·15
Undetermined substance.....	6·20
	100·00

The deficiency in the analysis is attributed by the author to the presence of phosphorus, nitrogen, or perhaps hydrogen. Insufficiency of material is offered as an apology for the incompleteness of the investigation. The origin of the mineral is not known.

J. W.

**Examination of the Meteorites which fell on July 23rd, 1872, at Lancé and at Authon (Loir-et-Cher).** By M. A. DAUBRÉE (Compt. rend., lxxv, 465—468).

Two meteorites fell on the 23rd of July, one at Lancé near Saint-Amand (Loir-et-Cher), the other at Authon, 12 kilometers ( $7\frac{1}{2}$  miles) from Lancé. That they were fragments of the same bolide is shown by their analysis as well as by their history.

The former weighed 47 kilograms (104 lbs.). It had rounded surfaces cut by two planes slightly inclined to each other, such as might be produced by fracture and the removal of a portion of an



irregular spheroid. The whole was covered by a fused crust, probably the result of incandescence during the passage of the meteorite through the earth's atmosphere. The other meteorite was smaller than the first. The surface of the meteorites displayed by fracture was of a dark-grey colour. They had a granular structure, and throughout small grains, colourless, or of a greenish-yellow hue, were discernible. Grains of a brilliant metallic lustre, like ferrous sulphide, were also seen, and on polishing, small grains of iron-grey colour became visible. On trituration the latter were found to be malleable and hammered out into little plates. A thin transparent plate of the substance when examined with the microscope, exhibited doubly refracting crystals.

The density of the substance was 3·80.

*Analysis.*—On treating the substance with water, chloride of sodium was dissolved out. The quantity found was 0·12 per cent.; and it was proved that the chloride of sodium really belonged to the meteorite itself, and was not introduced after the body fell upon the ground. A determination of the chlorine by raising the substance to a red heat in a current of hydrogen confirmed the result as to amount. Salts of potassium, also sulphates and hyposulphites, were absent. Abundance of sulphuretted hydrogen was given off on treating with dilute hydrochloric or dilute sulphuric acid; but there was no simultaneous deposition of sulphur, which indicated that monosulphides alone were present. A determination of the sulphur of the sulphuretted hydrogen assisted in the estimation of the quantities of the native metals. An attackable silicate of magnesia and ferrous oxide was found present. Unattackable silicate was also found in large quantity. Copper was found, and calcium barium, and strontium were proved absent by means of the spectroscope.

The following are the results of the complete analysis:—

Free iron with nickel and cobalt.....	7·81	
Iron and other metals combined with sulphur	9·09	} 14·28
Sulphur.....	5·19	
Attackable silicates { Silica .....	17·20	} 42·44
{ Magnesia.....	13·86	
{ Ferrous oxide.....	11·33	
{ Manganous oxide .....	0·05	
Unattackable part.....	33·44	
Sodium chloride .....	0·12	
Water.....	1·24	

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99·33

J. T. B.

**Examination of the Meteorites of Ovifak, Greenland; with special reference to the Carbon and Soluble Salts which they contain.** By A. DAUBRÉE (Compt. rend., lxxv, 240—246).

In a previous communication it was stated that the meteorites discovered at Ovifak, belonged to at least three distinct types, and the

analytical results relating to the specimen representing the first of these types, were then detailed; the examination of the second and third types forms the subject of the present paper.

The substance of the second type was not homogeneous. On attempting to reduce it to powder, it separated into two portions; one of these powdered readily, but the other was fibrous, and was with difficulty brought to a state of fine subdivision. The metallic portion of the third type was also far from being homogeneous, and analysis showed that silicates were intimately disseminated throughout it. The silica in one specimen amounted to 11.9 per cent. of the total weight. In the following table the analyses of the three principal types are compared:—

	1st type.	2nd type.	3rd type.
Iron (metallic) .....	40.94	80.8	61.99
Iron (combined) .....	30.15	1.6	8.11
Carbon (combined) ....	3.00	2.6	3.6
Carbon (free).....	1.64	0.3	1.1
Silicon.....	0.75	0.29	—

The soluble salts in the meteorites were estimated by exhausting them with alcohol and water respectively; the following are the results:—

	1st type.	2nd type.	3rd type.
Calcium sulphate.....	1.288	0.053	0.047
„ chloride.....	0.039	0.233	0.146
Ferric chloride.....	0.027	0.089	0.114

Particular attention is directed to the presence of the above soluble salts, since they lend considerable weight in favour of the meteoric origin of these masses of iron.

Although it has been known for a long time that an exudation of drops of ferric chloride frequently takes place from the surface of meteoric irons, it has been customary to suppose that the chlorine was not an original constituent of the meteorite, but that it had been subsequently absorbed. The author is of opinion that this supposition is no longer tenable, not only on account of the evidence to the contrary brought forward on the present occasion, but because the accumulated evidence of independent observers, especially in America, tends in the same direction, namely, to prove that calcium chloride and other deliquescent salts are really to be considered as almost invariable constituents of meteoric stones. Now, inasmuch as the above salts are, as a rule, seldom if ever met with in terrestrial rocks, their presence under certain conditions affords strong presumptive evidence of the meteoric origin of any particular specimen.

The absence of sodium chloride in these masses is remarkable, since in their original position they were constantly moistened by sea-water. This circumstance, combined with the intimate dissemination of the chlorides throughout the inner substance of the iron of Ovifak, offers additional proof that these chlorides are not in any way to be ranked as adventitious constituents.

It has been noticed that these blocks of iron rapidly decompose when

removed to warmer latitudes, where the tension of aqueous vapour is considerable. This alteration is due to the deliquescence of the iron and calcium salts, which slowly but effectually cause the disintegration of the mass. Type No. 2, which was found to undergo alteration the most rapidly, contained also the largest proportion of calcium chloride.

The last section of the paper is devoted to some theoretical speculations respecting the probable constitution of the internal substance of the globe.

J. W.

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*The Corundum Region of North Carolina and Georgia, with description of two Gigantic Crystals of that Species.* By C. U. SHEPARD (American Journal of Science [3], iv, 107).

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*The Datolite from Bergen Hills, New Jersey.* By E. S. DANA (*ibid.*, 16).

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*Didymium in Pyromorphite.* By C. HORNE (Chem. News, xxvi, 109).

THE examination of some specimens of this mineral from Cumberland showed, by the intensity of the absorption bands, that it contained a quantity of didymium equal to that in asparagus stone.

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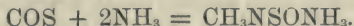
## Organic Chemistry.

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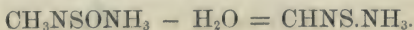
**Carbon Oxysulphide.** By BERTHELOT (Ann. Chim. Phys. [4], xxvi, 470—472).

HAVING had occasion to prepare the carbon oxysulphide recently described by Than, the author has studied some of its reactions.

Carbon oxysulphide is absorbed slowly by aqueous potash, but more rapidly than vapour of carbon bisulphide diffused through air or another gas. Bromine, hydrogen sulphate, potash moistened with alcohol, and absolute alcohol behave similarly towards carbon oxysulphide and carbon disulphide; ammonia, however, is a very suitable reagent for distinguishing between the two bodies. When ammonia and carbon oxysulphide are mixed, the sides of the containing vessel become immediately covered with a crystalline substance, which was found to be ammonium oxysulphocarbamate,  $\text{CH}_3\text{NSONH}_3$ .

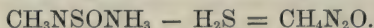


Ammonium oxysulphocarbamate heated with water to  $100^\circ$ , splits up into ammonium sulphocyanate and water.





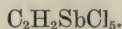
When very gently heated with water and lead carbonate, it yields a small quantity of urea, together with lead sulphide.



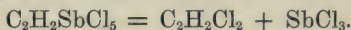
T. B.

**The Chlorides of Acetylene and the Synthesis of Julin's Chloride.** By BERTHELOT and JUNGFELEISCH (Ann. Chim. Phys. [4], xxvi, 472—477).

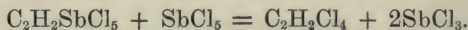
When dry acetylene is passed into antimony pentachloride, it is absorbed with a considerable rise of temperature. The chloride being saturated, care having been taken to prevent the temperature rising too high, it deposits on cooling magnificent plates which consist of a compound of acetylene and antimony perchloride.



This compound is immediately decomposed by water, and when it is heated by itself, an action takes place resulting in the formation of antimony trichloride and *acetylene dichloride*.



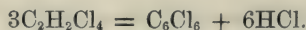
If, however, a solution of the crystals in antimony trichloride be heated a more violent action takes place, giving rise to the formation of antimony trichloride and *acetylene tetrachloride*.



In practice both chlorides are produced at the same time by heating the crude compound  $\text{C}_2\text{H}_2\text{SbCl}_5$  mixed with a certain proportion of antimony pentachloride, distilling, washing with water, and separating the chlorides by fractionation.

*Acetylene dichloride*,  $\text{C}_2\text{H}_2\text{Cl}_2$ , is a colourless limpid fluid, having an odour like chloroform, and boiling at about  $55^\circ$ . Water acts slowly on it at  $180^\circ$ , with formation of hydrochloric acid and condensed products. With potassium hydrate it forms acetic acid, and when it is heated to  $360^\circ$  in a sealed tube, it is entirely resolved into carbon and hydrochloric acid.

*Acetylene tetrachloride*,  $\text{C}_2\text{H}_2\text{Cl}_4$ , is a colourless liquid, in taste and smell resembling chloroform, and boiling at about  $147^\circ$ . Water at  $180^\circ$  slowly decomposes it with the formation of hydrochloric acid. Chlorine converts it into carbon trichloride. Treatment with alcoholic potash gives rise to glycollic acid, but when the action of this reagent is carefully controlled, no dichloroacetylene is obtained, but *chloroacetylene dichloride*,  $\text{C}_2\text{HClCl}_2$ , a colourless liquid boiling at  $88^\circ$ . When heated in a sealed tube to  $300^\circ$  for 15 hours, acetylene tetrachloride splits up into *chloroacetylene dichloride* and hydrochloric acid; but if the action be prolonged or the temperature be raised to  $360^\circ$  instead of dichloroacetylene, there is formed its polymeride, Julin's chloride—



This corresponds to the formation of benzene by the polymerisation of acetylene, and explains the frequent formation of Julin's chloride during the destructive distillation of chlorinated bodies.

T. B.

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**Nitrocarbol.** By H. KOLBE (J. pr. Chem. [2], v, 427—432).

THE author has made several attempts to obtain nitroacetic acid, but has hitherto been unsuccessful. One attempt made was by the action of a concentrated solution of potassium nitrite on monochloroacetic ether; action began at 100°, with evolution of a mixture of gases, carbonic anhydride, nitric oxide, and also a gas, which burnt with a yellowish white flame; the residue contained a salt, which has been described under the name of potassium oxalovinate (ætheroxalsäures Kali). A mixture of solutions of potassium monochloroacetate and nitrite becomes yellow when heated, and then turns brown, with strong evolution of gas (CO<sub>2</sub>). At the same time a heavy oil begins to distil off, which, after washing with water and drying, boils at 101°. On analysis it proved to have the composition CH<sub>3</sub>NO<sub>2</sub>. This compound is therefore isomeric with methylic nitrite, and must be considered as a nitration product of marsh-gas or nitrocarbol. From methylic nitrite it differs very much in its properties. The formation of nitrocarbol is easily explained, on the supposition that the yellow coloration indicates a change in the solution, attended with formation of potassium nitroacetate, which again decomposes into nitrocarbol and potassium carbonate (CH<sub>2</sub>NO<sub>2</sub>)CO<sub>2</sub>K + H<sub>2</sub>O = (CH<sub>3</sub>NO<sub>2</sub>) + CO  $\left\{ \begin{array}{l} \text{OK} \\ \text{OH} \end{array} \right.$ . By the action of ethylic iodide on silver nitrite, nitroethane is obtained, which may be looked upon as probably methylnitrocarbol. There can be little doubt that nitromethane, prepared by the action of silver nitrite upon methylic iodide, and nitrocarbol are identical. A series of researches in this direction, and on the action of potassium nitrite solutions on such bodies as chloropropionic acid, chloral, bromotyric acid, &c., has been commenced.

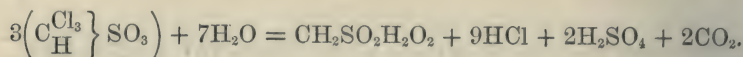
A. P.

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**A Product of the Decomposition of Chloromethyl-Sulphurous Acid.** By N. JAZUKOWITSCH (Zeitschr. f. Chem. [2], vii, 235).

DURING the preparation of potassium trichlormethyl-sulphite by the action of potassium hydrate on the chloride, the author noticed the constant formation of a potassium salt, but slightly soluble in water. This salt is yellowish, insoluble in alcohol, and separates as a crust when its aqueous solution is evaporated. It contains no water of crystallisation, is neutral, and is not decomposed at 150°. When, however, it is more strongly heated, it is carbonized, and the residue contains potassium sulphide and sulphite. Barium chloride gives in its neutral or acid solution a precipitate of barium sulphate. Silver nitrate gives no precipitate in the solution made acid by nitric acid. Analysis led to the formula, CH<sub>2</sub>SO<sub>2</sub>K<sub>2</sub>O<sub>2</sub>.

The same body was obtained by heating potassium trichlor-methylsulphite with potassium hydrate and water, to  $100^{\circ}$ — $120^{\circ}$ , also by the action of potash-solution on potassium mono- and dichlormethyl sulphite :



Attempts to obtain the free acid  $\text{CH}_2\text{SO}_2\text{H}_2\text{O}_2$  were unsuccessful. The author considers that perhaps this acid is a homologue of isethionic acid.

T. B.

### **Thioisopropylalcohol and Isopropylsulphonic Acid.** By AD. CLAUS and DR. KEERL (Deut. Chem. Ges. Ber. v, 659).

PURE isopropyl iodide is mixed with an alcoholic solution of potassium sulphhydrate, and after the mixture has stood some time in the cold, it is slowly heated on the water-bath, and about one-half distilled over. If the mixture be heated at once, but little mercaptan is obtained, but in place of it a less volatile oil, which, even under the most favourable conditions, constitutes at least a fourth part of the crude product. The above distillate is mixed with water, the oil which separates is dried and rectified, and the portion boiling between  $56^{\circ}$ — $65^{\circ}$  is collected apart. By fractional distillation, the main bulk of this is obtained, boiling at  $57^{\circ}$ — $60^{\circ}$ , but it is impossible to obtain a purer product, since it is partially decomposed, with evolution of sulphuretted hydrogen on distillation.

Thioisopropyl alcohol is violently acted upon by concentrated nitric acid, and converted into isopropyl-sulphonic acid,  $\text{C}_3\text{H}_7\text{SO}_2\text{OH}$ . The potassium salt of this same acid is obtained by the action of isopropyl iodide on potassium sulphite. It yields a series of well crystallised salts.

H. E. A.

### **Transformation of Allyl Alcohol into Normal Propyl Alcohol.**

By B. TOLLENS (Zeitschr. f. Chem. [2], vii, 249).

THE author has already shown that the action of potassium hydrate on allyl alcohol gives rise to a mixture of alcohols, which, when converted into bromides and fractionated, splits up into ethyl and propyl bromides. In order to study the propyl compound more accurately, a portion of the mixed alcohols was converted into acetates, and the propyl acetate separated by fractionation. It boiled at  $100^{\circ}$ — $102^{\circ}$ , and when oxidised yielded propionic acid, with a trace of a substance smelling like aldehyde, but scarcely any carbonic acid. The author has thus confirmed his previous statement, that by fusion with potassium hydrate, allyl alcohol yields normal propyl alcohol free from isopropyl alcohol. This supports the conclusion that allyl alcohol is a primary alcohol.

The high boiling point portions of the mixture of alcohols yielded, after conversion into acetates, fractions boiling between  $155^{\circ}$ — $165^{\circ}$ , and  $195^{\circ}$ — $205^{\circ}$ , which gave numbers agreeing tolerably with the



formulae,  $C_2H_3(C_6H_{11})O_2$  and  $C_2H_3(C_9H_{13})O_2$ , thus indicating the presence of either mesityl oxide and phorone, or their isomerides in the mixture of alcohols.

During the action of potassium hydrate on allyl alcohol, the author has noticed the production of formic acid, and he believes that of propionic acid, also that of acids yielding uncrystallisable salts. The acid boiling at  $230^\circ$ – $270^\circ$  gave by analysis numbers agreeing with the formula  $C_9H_{14}O_2$ , but the analysis of its salts led to the formula,  $C_8H_{14}O_3$ .

T. B.

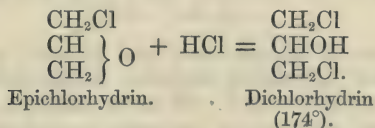
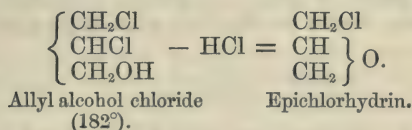
**The Oxidation of Allyl Alcohol.** By RINNE and TOLLENS (Zeitschr. f. Chem. [2], vii, 250).

WHEN allyl alcohol is oxidised by means of potassium bichromate and sulphuric acid, a strong odour of acrolein is produced, and the mixture on distillation yields formic acid. No acetic acid was detected, and the formation of acrylic acid, though probable, was neither definitively proved nor disproved.

T. B.

**Transformation of Allyl Alcohol Chloride into the Isomeric Dichlorhydrin.** By MÜNDER and TOLLENS (Zeitschr. f. Chem. [2], vii, 252).

ALLYL alcohol chloride, boiling at  $182^\circ$ , when treated with potassium hydrate, yields epichlorhydrin, boiling at  $115^\circ$ – $118^\circ$ , and this by the action of hydrochloric acid, becomes converted into dichlorhydrin, boiling at  $172^\circ$ – $174^\circ$ .



T. B.

**Transformation of Dichlorhydrin boiling at  $174^\circ$  into the isomeric compound boiling at  $182^\circ$ .** By HÜBNER and MÜLLER (Zeitschr. f. Chem. [2], vii, 232).

ALLYL alcohol prepared by the action of sodium on dichlorhydrin boiling at  $174^\circ$ , was reconverted into dichloride by treatment with chlorine. The dichloride thus prepared was found to be identical with that which Tollens obtained by the combination of chlorine with the alcohol prepared from glycerin and oxalic acid.

In order to prove the presence of hydroxyl in the dichlorhydrin

boiling at  $182^{\circ}$ , it was converted into trichlorhydrin by the action of phosphoric chloride.

T. B.

**Dextrin.** By MUSCULUS (Bull. Soc. Chim. [2], xviii, 66).

THE author appears to have formed dextrin by the dehydration of glucose. Proceeding on the view that dextrin is the ether of glucose, he prepared sulphoglucosic acid by dissolving dry glucose in concentrated sulphuric acid, mixed this with alcohol of  $95^{\circ}$ , in which dextrin is very nearly insoluble, and set the mixture aside. A deposit, apparently dextrin, continued to form for about three weeks. Freed from adhering acid and alcohol, it possessed the following properties:—It was gummy while moist; amorphous and friable when dry: it was very soluble in water, insoluble in alcohol; had no sweet taste; did not reduce copper salts; was only very slightly saccharified by diastase; was slowly converted into glucose by boiling with dilute sulphuric acid; and was not coloured by iodine. Its rotatory power, however, although very nearly double that of glucose, was still far below that of ordinary dextrin.

E. D.

**Cellulose and Tunicin.** By BERTHELLOT (Bull. Soc. Chim. [2], xviii, 9).

THE different principles to which the name *cellulose* has been attached are distinguished from one another by the different resistances they oppose to the action of acids or potash. Perhaps the most stable variety is *tunicin*, which is also not even carbonized by fluoride of boron.

C. G. S.

**Pyruvin.** By SCHLAGDENHAUFFEN (Bull. Soc. Chim. de Paris [2], xvii, 301—304).

FOUR combinations of tartaric acid and glycerin are already known, which are obtained by heating mixtures of the two bodies to temperatures ranging from  $100^{\circ}$ — $140^{\circ}$ . When a mixture of equal quantities of tartaric acid and glycerin is gradually heated for three days up to  $200^{\circ}$  in a retort, a small quantity of crystals sublimes in the neck, and a small quantity of a watery distillate is obtained also containing some of this crystalline body. On analysis this is found to have the com-

position  $C_6H_{10}O_5$ , and is proved to have the rational formula  $\left. \begin{array}{l} C_3H_5 \\ H_2 \\ C_2H_3O_2 \end{array} \right\} O_3$ ,

by the action of water and of alkalis, which convert it into glycerin and pyruvic acid.

The glyceride is a crystalline white body, without action on litmus-paper; it melts at  $78^{\circ}$ , and boils, with decomposition, at  $242^{\circ}$ . It is soluble in alcohol, ether, turpentine, and in carbon disulphide, from which it has been obtained in crystals 7 centimeters long. It is

gradually decomposed by cold and rapidly by hot water and by the alkalis, yielding pyruvic acid and glycerin. It does not precipitate metallic salts, such as iron, lead, copper, and silver, either in hot or in cold solutions.

A. P.

**Remarks on Isobutyl Aldehyde.** By ANTON PFEIFFER (Deut. Chem. Ges. Ber., v, 699).

ISOBUTYL aldehyde was obtained by cautiously oxidising isobutyl alcohol with chromic acid solution mixed with sulphuric acid to dissolve the chromic hydrate produced, 100 grams of the alcohol,  $\frac{3}{4}$  litre of water, 95 grams of chromic acid, and about 90 c.c. of strong sulphuric acid being employed, and the mixture being only gently warmed. On re-distillation of the distillate in the water-bath, isobutyl isobutyrate was left, and the aldehyde distilled over. After treatment with sodium bisulphite (whereby crystals were formed), and drying over calcium chloride, the aldehyde boiled constantly at  $61^{\circ}$ .

Ammonia gave a difficultly crystallisable compound. Potash appeared to polymerize the aldehyde, forming a yellow liquid of peculiar aromatic odour, boiling for the most part at  $145^{\circ}$ — $155^{\circ}$ .

Sulphuretted hydrogen produced with isobutyl aldehyde an oil which could not be converted into a crystalline body, and had an abominable alliaceous odour. This product distilled with water, but could not be obtained in a state fit for analysis. With an aqueous solution of the aldehyde-ammonia, sulphuretted hydrogen gave an amorphous mass only rendered crystallisable with great difficulty; this is *isobutyraldine*,  $C_{12}H_{25}NS_2$ . It formed with mercuric chloride a compound nearly insoluble in water, amorphous to the naked eye, but crystalline under the microscope.

When shaken with carbon bisulphide after saturation with concentrated ammonia, isobutyl aldehyde formed *carboisobutyraldine*,  $C_9H_{16}N_2S_2$ : this was crystallisable and soluble in alcohol and ether, but not in water, and melted at  $91^{\circ}$ .

C. R. A. W.

**Note on Mesoxalic Acid.** By J. OSSIKOVSKY and G. BARBAGLIA (Deut. Chem. Ges. Ber., v, 667).

THE authors have sought to convert chloroxalic ether,  $\begin{matrix} \text{COCl} \\ \text{CO.OC}_2\text{H}_5 \end{matrix}$ , into mesoxalic ether, but unsuccessfully.

They find that cyanoxalic ether,  $\begin{matrix} \text{COCN} \\ \text{CO.OC}_2\text{H}_5 \end{matrix}$ , is readily decomposed in presence of water or alcohol into oxalic and hydrocyanic acids and alcohol.

*Acetyloxamic ether*,  $\begin{matrix} \text{CO.HN.CO.CH}_3 \\ \text{CO.OC}_2\text{H}_5 \end{matrix}$ , was obtained by the action of acetamide on chloroxalic ether. It is probably a crystalline compound. It is decomposed on distillation, and is resolved on heating with water into ethyl acetate and hydrogen ammonium oxalate.

H. E. A.



**Preliminary Notice on Acryl Compounds, &c.** By E. LINNEMANN  
(Ann. Chem. Pharm., clxiii, 369—370).

1. THE sodium salt prepared from acrylic acid purified by fractional distillation, is unaltered by exposure to the air. The aqueous solution of the silver salt may be boiled and even evaporated to dryness at  $100^{\circ}$  without reduction of the silver. Two different basic lead salts exist which are soluble in water, and the normal lead salt contains water of crystallisation which is not removed by drying over sulphuric acid.

2. The product of the spontaneous change of acrylic acid swells up in alcohol and in water, and bears a close resemblance to the paradipimalic acid of Wislicenus in its behaviour with metallic salts; an analysis of its lead salt, however, showed that it had a different composition.

3. The ethyl chloropropionate prepared from acrylic acid, yields, with ammonia, a *dilactamic acid*, which appears to be identical with the acid prepared by Heintz from iodopropionic acid. This ethyl chloropropionate differs from that obtained from glyceric acid, as it is decomposed and its chlorine removed by treatment with baryta water.

4. *Tetrallylammonium bromide* combines with eight, and allylamine with two atoms of bromine; the latter compound is a base, and is reconverted into allylamine by treatment with sodium amalgam.

5. Hydrochloric acid combines directly with *chlorallyl*, forming propylene chloride, and the acid has a similar action on *iodallyl*, although much isopropyl iodide is formed at the same time.

C. E. G.

**The most Volatile Coal-oils, and Dinitrobenzene.** By  
ROMMIER (Bull. Soc. Chim. [2], xviii, 70).

THE author has examined the most volatile portions of commercial benzene for Carius's *pentene*,  $C_5H_4$ , the lower homologue of benzene, and obtained by distilling Church's benzenic acid,  $C_6H_4O_2$ , with lime; but he has failed to detect it. The oils boiling at  $40^{\circ}$ — $50^{\circ}$  consist almost entirely of carbon bisulphide.

Dinitrobenzene is very easily purified by two crystallisations from boiling water. It forms long white needles, very flexible while moist, and melting at  $84.5^{\circ}$ .

E. D.

**Mesitylene.** By ROMMIER (Bull. Soc. Chim. [3], xviii, 71).

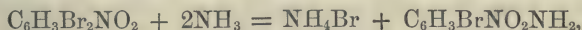
HAVING already established that the mesitylene in coal oils is insoluble in hot sulphuric acid of the ordinary strength, and that the cumene dissolves in it and can be obtained pure from it by distillation, the author wished to ascertain whether the cumene thus obtained might not have been derived from mesitylene which had dissolved and become modified. He now finds that mesitylene dissolves in fuming sulphuric acid, from which it can be separated unchanged by distillation. It can thus be obtained from coal oils perfectly pure.

E. D.

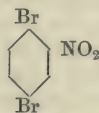
**Some Derivatives of the Solid Dibromobenzene.** By MEYER and WURSTER (Deut. Chem. Ges. Ber., v, 632—636).

As Walker and Zincke (*ibid.*, v, 114) had found that nitraniline was obtained by heating monobromonitrobenzene with alcoholic ammonia, the authors thought it possible that nitrated dibromobenzene, by similar treatment, might yield a nitrated phenylene-diamine; this, however, was found not to be the case

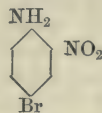
*Action of Ammonia on Nitrodibromobenzene.*—The nitro-product,  $C_6H_3Br_2NO_2$ , prepared by boiling dibromobenzene with fuming nitric acid, when heated with concentrated alcoholic ammonia for several hours to  $200^\circ$ — $210^\circ$ , yields a black liquid. This is poured into hydrochloric acid, separated from the resin, and the red-brown solution poured into water. The new compound now separates in the form of fine interlaced needles of an orange colour, which may be purified by crystallisation from ether, repeated solution in hydrochloric acid, and reprecipitation by water. On analysis the substance was found to be a bromonitramidobenzene,  $C_6H_3BrN_2O_2$ ,



from which the remaining atom of bromine could not be removed, even by long digestion with alcoholic ammonia at a very high temperature. Bromonitramidobenzene crystallises in fine orange-coloured needles, which melt at  $104.5^\circ$ , sublime without decomposition, and volatilise readily in the vapour of water. It is freely soluble in alcohol and ether, slightly soluble in cold water, and somewhat more so in hot water, yielding a yellow solution. Although the substance possesses no basic properties, it dissolves in concentrated hydrochloric or nitric acid, and is reprecipitated on the addition of water. Its hot aqueous solution dyes silk and wool a fine yellow colour. With regard to the constitution of this compound, the authors believe that, as the solid dibromobenzene is 1 : 4, the nitro compound must be 1 : 2 : 4, and the amido compound will therefore have the constitution represented below—



Nitrated dibromobenzene.



Amidonitrobenzene.

As the  $NO_2$  group in the amidonitrobenzene is next to the  $NH_2$  group, the authors determined to prepare the bromophenylene-diamine from it, which would thus have two  $NH_2$  groups in close proximity, and then to debrominate this by sodium-amalgam and compare the resulting phenylene-diamine with the three at present known.

*Phenylene-diamine from Bromonitramidobenzene.*—On treating the bromonitramidobenzene with tin and concentrated hydrochloric acid, adding excess of soda, and agitating the product with ether, the bromophenylene diamine is dissolved, and left again on evaporation of the ethereal solution as a thick liquid, which solidifies over sulphuric acid, to a reddish crystalline mass. With hydrochloric acid it forms a crystalline

salt, which is insoluble in the concentrated acid, and rapidly acquires a red colour on exposure to the air. The base was debrominated by treatment with water and a large excess of sodium-amalgam, and the phenylene-diamine extracted from the product by agitation with ether. When purified it was found to have the formula,  $C_6H_4(NH_2)_2$ , and to melt at  $99^\circ$ , being identical in its reactions and characters with the phenylene-diamine melting at  $99^\circ$  discovered by Griess (*ibid.* v, 201). This confirms the opinion of Griess, that the phenylene-diamine melting at  $99^\circ$ , has the  $NH_2$  groups united to neighbouring carbon-atoms. Although no odour of quinone was observed on oxidizing this phenylene diamine, the authors do not feel justified in drawing any conclusion from this circumstance as to the constitution of quinone.

C. E. G.

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**Benzylethylbenzene.** By J. T. WALKER (Deut. Chem. Ges. Ber., v, 686—687).

THIS hydrocarbon is produced, together with other bodies, by boiling a mixture of benzyl chloride, ethyl-benzene, and zinc, as long as hydrochloric acid is given off, and isolated from the product by fractional distillation. *Benzylethylbenzene*,  $C_6H_5.CH_2.C_6H_4.C_2H_5$ , is a colourless liquid, boiling at  $294^\circ$ — $295^\circ$ , and possessing a faint aromatic smell. On oxidation it yields benzoyl-benzoic acid, together with a ketone, which has not been obtained in a pure state.

C. S.

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**Derivatives of Benzyltoluene.** By TH. ZINCKE (Deut. Chem. Ges. Ber., v, 683—686).

THIS hydrocarbon is violently acted upon by bromine, even when dissolved in carbon bisulphide, but it was not possible to isolate a definite compound from the product. Concentrated nitric acid converts it into *dinitrobenzyltoluene*,  $C_{14}H_{12}(NO_2)_2$ , a large quantity of a resinous body being formed at the same time. The dinitro-compound crystallises from hot alcohol in slender white needles, or on slowly cooling in thin prisms, and by the spontaneous evaporation of the solution it was obtained in brilliant prisms, melting at  $137^\circ$ . By the action of tin and hydrochloric acid it is reduced to *diamidobenzyltoluene*, forming a tin-double salt which crystallises in small and very soluble needles. The hydrochloride,  $C_{14}H_{12}(NH_2)_2 \cdot 2ClH$ , is very soluble in water and alcohol, and can be purified only by recrystallisation from hot dilute hydrochloric acid; it forms white needles or plates. The sulphate  $C_{14}H_{12}(NH_2)_2 \cdot SO_4H_2$ , is also very soluble, and crystallises from hot alcohol in long colourless needles. By decomposing the hydrochloride with potash, the free base is obtained as a white crystalline powder. It is freely soluble in alcohol and ether, and the solution darkens when exposed to the air. If instead of concentrated nitric acid, an acid of sp. gr. 1.4 is used, the action begins only on a water-bath; nitrous fumes are evolved, and besides nitration, oxidation also takes place, the chief product being a compound containing  $C_{14}H_{11}(NO_2)O$ . This body is probably *nitromethylbenzophenone*,  $C_6H_4(NO_2)-CO-C_6H_4-CH_3$ .



It crystallises from hot dilute alcohol in long flat needles, or silky plates, melting at  $127^{\circ}$ , and subliming without decomposition in shining plates. When treated with tin and hydrochloric acid, it yields an amido-compound, forming amorphous salts, from which it is precipitated by soda-solution as a light white powder.

*Tetranitrobenzyltoluene*,  $C_{14}H_8(NO_2)_4$ , is obtained, together with resinous bodies, by acting on the hydrocarbon with a mixture of highly concentrated nitric acid and concentrated sulphuric acid. It crystallises from hot benzene or chloroform in small but well-defined prisms, melting at  $160^{\circ}$ — $161^{\circ}$ , and deflagrating at a higher temperature.

Benzyltoluene dissolves in hot fuming sulphuric acid, with formation of at least two sulpho-acids; but only the disulpho-acid could be isolated, its potassium salt being almost insoluble in strong alcohol, and crystallising from hot dilute alcohol in white laminae or broad needles, having the composition  $C_{14}H_{12}(SO_3K)_2 + 3\frac{1}{2}H_2O$ , and being readily soluble in water. The barium salt,  $C_{14}H_{12}(SO_3)_2Ba + 8\frac{1}{2}H_2O$ , separates from an aqueous solution on addition of alcohol in crystalline crusts, which redissolve in water but slowly. The copper salt,  $C_{14}H_{12}(SO_3)_2Cu + 4\frac{1}{2}H_2O$ , crystallises from a hot concentrated solution in small bluish green laminae, and from dilute alcohol in prisms. The lead salt is readily soluble in hot water, sparingly in cold, and forms colourless prisms. The free acid is easily soluble in water, alcohol, and ether, and forms a crystalline mass, consisting of long colourless needles, melting at  $38^{\circ}$ .

C. S.

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**Diphenyl.** By G. SCHULTZ (Deut. Chem. Ges. Ber., v, 682).

THIS hydrocarbon was prepared according to the methods of Fittig and of Berthelot; the former gives the largest yield, but the latter is more convenient, and works more quickly. By acting on the hydrocarbon with a solution of chromic acid in glacial acetic acid, it is oxidised to benzoic acid.

*Monobromodiphenyl*,  $C_{12}H_9Br$ , is formed by adding bromine to a solution of the hydrocarbon in carbon disulphide. It crystallises in laminae, melting at  $89^{\circ}$ , and boiling at  $310^{\circ}$ , and yields on oxidation parabromobenzoic acid. The same acid is produced by oxidising *dibromodiphenyl*. Diphenyl does not combine with hydrogen when it is heated with concentrated hydriodic acid and phosphorus in sealed tubes to  $280^{\circ}$ .

C. S.

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**$\alpha$ -Bromo-sulpho-toluene and  $\alpha$ -Sulphotoluene.** By HÜBNER and TERRY (Zeitschr. f. Chem. [2], vii, 232).

CRYSTALLISED bromotoluene when completely separated from the fluid bromotoluene, melted at  $28^{\circ}$ — $29^{\circ}$ , boiled at  $185^{\circ}$ , and had a specific gravity of 1.3999 at  $30^{\circ}$ . When dissolved in fuming sulphuric acid, it gave, on neutralization, a calcium salt  $(C_6H_3.CH_3Br.SO_3O)_2Ca + 4H_2O$ , crystallising in long needles. The free acid separated from this salt by sulphuric acid formed a mass of leaf-like crystals easily soluble in

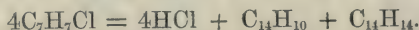
water and alcohol, but only slightly soluble in ether. The acid was converted into the  $\alpha$ -barium salt, then into the  $\alpha$ -copper salt, which differs from the  $\beta$ -salt by its greater solubility, and from this it was set free by the action of hydrosulphuric acid. This acid is not altered by being heated to  $210^\circ$ , and yields, whether previously heated to  $210^\circ$  or not, the same amide as that yielded by the acid prepared from the sodium salt, having the composition  $C_6H_3.CH_3.Br.(SO_2ONa) + \frac{1}{2}H_2O$ , and crystallising from alcohol in monoclinic tables. This amide,  $C_6H_3.CH_2.Br.(SO_2NH_2)$ , melts at  $260^\circ$ — $267^\circ$ , and crystallises from water in long needles.

The acid obtained from the  $\alpha$ -copper salt yielded on treatment with sodium-amalgam,  $\alpha$ -sulphotoluene,  $C_6H_4.CH_3.SO_2OH$ , which forms a mass of large foliated crystals. *Lead salt*,  $(C_6H_4.CH_3.(SO_2O)_2Pb + 4H_2O$  : needles very soluble in alcohol and water. *Barium salt*,  $(C_6H_4.CH_3.(SO_2O)_2Ba + HO$  : monoclinic tables, very soluble. *Calcium salt* : needles exceedingly soluble in water and alcohol. *Potassium salt*,  $C_6H_4.CH_3.(SO_2OK) + H_2O$  : very soluble, efflorescent, monoclinic tables. The amide forms monoclinic prisms, very soluble in water, and melting at  $152^\circ$ — $153^\circ$ .

The authors are engaged in the examination of the oxidation-products of these acids. T. B.

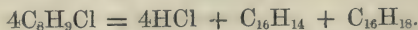
**Dimethylantracene.** By A. VAN DORP (Deut. Chem. Ges. Ber., v, 674—676).

It is well known that Limpricht obtained anthracene by heating benzyl chloride with water under pressure:—



The author has submitted the homologous compound, *xylyl chloride*,  $C_6H_4 \begin{smallmatrix} CH_3 \\ | \\ CH_2 \end{smallmatrix} Cl$  (boiling point  $190^\circ$ — $200^\circ$ ) prepared by the action of chlorine on boiling coal-tar xylene,\* to the action of water in sealed tubes at  $200^\circ$ . It is thus converted into a brown oil of aromatic odour of which but little passed over on distillation below  $230^\circ$ ; the thermometer then rose gradually to the boiling point of mercury, and a pale yellow oil distilled over; at a later stage, a crystalline body condensed in the neck of the retort, after which came semi-solid products.

The crystalline substance is dimethylantracene,  $C_{16}H_{14}$ . Its formation may be expressed by the equation:



The above-mentioned oil is probably the compound  $C_{16}H_{18}$ , since it is almost entirely converted into  $C_{16}H_{14}$  on passing it through a red-hot tube, and at the same time hydrogen is evolved.

Dimethylantracene closely resembles anthracene; it crystallises in large glistening plates, which are white and fluorescent when perfectly pure, and melt at about  $200^\circ$ . Oxidised by chromic acid, it yields a

\* The xylene employed gave chiefly *iso*- and but little terephthalic acid on oxidation.

product which may be sublimed in yellow plates melting at  $153^{\circ}$ , which is probably dimethylantraquinone. A small quantity of a second body of higher melting point is also formed.

H. E. A.

**Mononitroresorcin.** By P. WESELSKY (Ann. Chem. Pharm., clxiv, 1—8).

WHEREAS trinitroresorcin is readily formed by the action of a mixture of nitric and sulphuric acids on resorcin (Stenhouse), the author did not succeed in obtaining *mono-* or *di-nitroresorcin* by direct nitration. Mononitroresorcin is formed, however, as a secondary product in the preparation of diazoresorcin (this *Journal* [2], ix, 830). On distilling off the ether after the azo-compound is deposited, a dark-coloured resinous mass remains. This is boiled with much water, the solution filtered, and the filtrate treated with lead acetate; the precipitate thus formed is removed; the lead in solution precipitated by sulphuric acid; and the filtrate shaken up with ether. To purify the crude mononitroresorcin which remains on distilling off the ether, it is dissolved in water and neutralised by baryta-solution; on cooling, a barium salt of the composition,  $C_6H_3(NO_2)O_2Ba + 5aq.$ , crystallises out in brilliant needles of the colour of potassium bichromate. The aqueous solution of this salt is acidulated with sulphuric acid and shaken up with ether; the ether is then distilled off, and the residue recrystallised from boiling water, from which the pure mononitroresorcin separates on cooling in the form of long, hair-fine, lemon-yellow needles, melting at  $115^{\circ}$ .

On passing a current of carbonic anhydride through a hot solution of the above barium salt, barium carbonate is precipitated, and, on cooling, a second salt of the formula,  $(C_6H_3(NO_2)OH.O)_2Ba + aq.$  crystallises out in small groups of fine dark golden-yellow needles. If a solution of the first salt be mixed with acetic acid, a third salt of the composition,  $(C_6H_3(NO_2)OH.O)_2Ba.C_6H_2(NO_2)(OH)_2 + 2aq.$ , is obtained; this crystallises in brilliant golden-yellow needles.

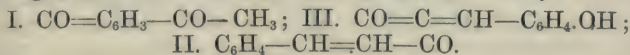
*Monoamidoresorcin hydrochloride* is obtained by reducing the mononitro-compound with tin and hydrochloric acid; it crystallises in large colourless, oblique prismatic forms.

*Dibromonitroresorcin* is produced when bromine is added to an ethereal solution of nitroresorcin, also by the action of nitric acid containing nitrous acid on tribromoresorcin; it crystallises from aqueous alcohol in golden-yellow, glistening plates, which melt at  $147^{\circ}$ .

H. E. A.

**On the Constitution of Coumarin.** By HUGO SCHIFF (Deut. Chem. Ges. Ber., v, 665—666).

OF the three formulæ proposed for coumarin by Perkin (I), Strecker and Fittig (II), and Baesecke (III) respectively, namely:—



O



the author considers the second to be in complete accordance with the known reactions of this body, and quotes the following facts, which cannot well be reconciled either with I or with III.

Lieben's experiments have shown that a large number of bodies in which the  $\text{CH}_3\text{—CO—C}$  grouping (I) exists, yield iodoform on treatment with iodine and potassium hydrate; coumarin, however, does not.

Neither does coumarin give a coloration with ferric chloride, as it should, according to III, but, what is of more importance, this formula also requires that it should yield an acetyl-derivative: the author finds, however, that both acetic anhydride and acetyl chloride are without action on coumarin.

H. E. A.

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**Aromatic Additive Compounds.** By C. GRAEBE (Dent. Chem. Ges. Ber., v, 677—681).

THE compounds obtained by the addition of hydrogen to aromatic compounds have been but little examined, with the exception of dihydranthracene; but a more complete knowledge of them appears very desirable, as it will enable us to determine the constitution of oil of turpentine and the terpenes in general. Since Oppenheim and Barbier have succeeded in converting oil of turpentine into cymene, the former hydrocarbon has been generally regarded as dihydrocymene. But this view is opposed by several facts. The chemical properties of oil of turpentine are quite different from those of other additive hydrocarbons, and moreover it can be easily converted into compounds like pyroterebic acid, which do not belong to the aromatic group. The author has therefore commenced researches on these additive hydrocarbons.

*Naphthalene tetrahydride*,  $\text{C}_{10}\text{H}_{12}$ , has been obtained by Baeyer by heating naphthalene with phosphonium iodide. A more convenient method is to heat 10 grams of naphthalene, 3 of phosphorus, and 9 of hydriodic acid (b. p.  $127^\circ$ ) for 6—8 hours to  $220^\circ\text{—}250^\circ$ . Naphthalene tetrahydride boils at  $205^\circ$ , has a peculiar odour, and combines with picric acid. By passing its vapour through a red-hot tube, it is resolved into hydrogen and naphthalene. Oxidising agents convert it into phthalic acid, and concentrated nitric acid forms nitro-compounds, of which only picric acid could be isolated. When bromine is added to a solution of the hydrocarbon in carbon disulphide, hydrobromic acid is given off, and an oily product is formed, which on distillation is decomposed, with formation of hydrobromic acid, naphthalene, dihydride of naphthalene, and brominated bodies.

Naphthalene tetrahydride dissolves in cold concentrated sulphuric acid, the monosulpho-acid being produced, which forms crystals readily soluble in water and alcohol. The barium salt,  $(\text{C}_{10}\text{H}_{11}\text{SO}_3)_2\text{Ba} + 2\text{H}_2\text{O}$ , crystallises in plates, dissolving freely in hot water and alcohol. The sodium salt,  $\text{C}_{10}\text{H}_{11}\text{SO}_3\text{Na} + \text{H}_2\text{O}$ , is readily soluble in water and alcohol. On fusing it with caustic potash it yields a phenol, and with sodium formate an acid.

*Cynene*,  $\text{C}_{10}\text{H}_{16}$ .—Voelcker obtained this hydrocarbon by the action

of phosphorus pentoxide on oil of wormseed, but it is more conveniently prepared by distilling this oil with phosphorus pentasulphide. It boils at  $174^{\circ}$ — $175^{\circ}$ , and yields, on oxidation with chromic acid solution, terephthalic acid, and not phthalic acid, as Kraut has stated. Cynene differs from oil of turpentine in dissolving in cold concentrated sulphuric acid without coloration, or evolution of sulphur dioxide, *cynene-sulphonic acid*,  $C_{10}H_{15}SO_4H$ , being formed. The free acid forms a thick syrup; its salts are readily soluble in water and alcohol. By fusing it with potash, oxidation takes place, and a liquid, *cymophenol*,  $C_{10}H_{13}OH$ , is formed, boiling at  $232^{\circ}$ — $235^{\circ}$ , and probably identical with that obtained by Mueller and Pott from cymenesulphonic acid. From these reactions it would appear that cynene is the dihydride of cymene, and it was therefore tried to reduce cymene to cynene.

By heating cymene with hydriodic acid and phosphorus to  $280^{\circ}$ — $290^{\circ}$  for 16 hours, a mixture of unaltered cymene and a hydro-compound is obtained, the chief portion of which boils at  $170^{\circ}$ — $176^{\circ}$  (the cymene boiling at  $175^{\circ}$ — $176^{\circ}$ ). This product, as well as the small portion boiling at about  $160^{\circ}$ , were acted upon by sulphuric acid like cynene.

C. S.

**Terpene Dibromide**,  $C_{10}H_{16}Br_2$ . By BIEDERMANN and OPPENHEIM (Deut. Chem. Ges. Ber., v, 627—628).

As hydrobromic acid is readily eliminated from terpene dibromide, it was resolved to study the action of oxidising agents on it. Although readily attacked by nitric acid, it only yields a resinous body, from which no definite nitro-compound could be isolated. A better result, however, is obtained by digesting it with acid potassium chromate and sulphuric acid. The solid product, after purification by repeated solution in soda and reprecipitation, was found to consist of terephthalic acid,  $C_8H_6O_4$ . A small quantity of a colourless body found in the upright condenser, the author believes to have been the monobromhydrate of turpentine oil,  $C_{10}H_{17}Br$ . It had an odour resembling that of camphor, and melted at  $60^{\circ}$ . The reaction would therefore seem to consist of the splitting up of the dibromide into hydrobromic acid and cymene, and the oxidation of the latter to terephthalic acid.

C. E. G.

**Cymene from Turpentine and from Lemon Oil.** By A. OPPENHEIM (Deut. Chem. Ges. Ber., v, 628—631).

THE object of this research was, if possible, to obtain some insight into the constitution of the isomeric ethereal oils by studying the cymenes obtained from them by the abstraction of a molecule of hydrogen. The terpene and citrene, boiling at  $160^{\circ}$ — $161^{\circ}$  and  $173^{\circ}$ — $174^{\circ}$  respectively, were first converted into the dibromides by the cautious addition of a molecule of bromine to the well cooled oils. After numerous trials, the author found that the best method of eliminating the two molecules of hydrobromic acid from these bromides was to heat them with a slight excess of aniline to  $180^{\circ}$  for eight hours: by this process a yield of 30 per cent. of the theoretical amount of

cymene was obtained. The boiling point of the hydrocarbon, from either source, was between  $176^{\circ}$  and  $179^{\circ}$ , and by oxidation with potassium dichromate and sulphuric acid it yielded terephthalic acid and acetic acid, showing that in both the cymenes the side chains consist of ethyl and normal propyl, and that their relative position is the same. The two cymenes would therefore appear to be identical, and terpene and citrene to consist of the same cymene combined with two atoms of hydrogen, differing from each other only in the relative position of the latter. It must be remembered, however, that the yield of terephthalic acid is much less than that indicated by theory, so that the acetic acid may be produced by the oxidation of a portion of the aromatic compound, and not of the side chain.

C. E. G.

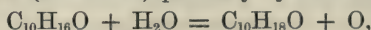
**Artificial formation of Camphor.** By OPPENHEIM (Deut. Chem. Ges. Ber., v, 631—632).

DURING some experiments made to determine whether the cymene from turpentine consisted of several isomeric modifications or only one, the author completely oxidised some of the former hydrocarbon, and obtained in the upright condensing tube a small quantity of a white crystalline substance having the appearance, odour, and composition of camphor. It sublimed readily, and melted at  $162^{\circ}$ , which is nearly the same melting point as that of camphor ( $176^{\circ}$ ), the difference being probably due to the presence of a small amount of impurity. A sublimate, having the same melting point was also obtained in the oxidation of the cymene from citrene. This compound does not appear to be produced under the same circumstances from turpentine; neither did terpene dibromide yield it by treatment with silver oxide or with silver salts.

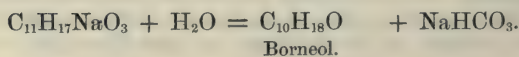
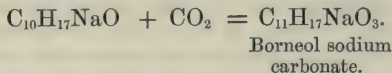
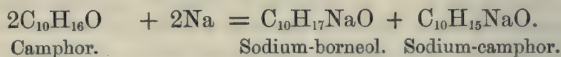
C. E. G.

**Compounds of the Camphor Group.** By J. KACHLER (Ann. Chem. Pharm., clxiv, 75).

WHEN an alcoholic potash-solution acts on camphor, a small quantity of borneol is formed (Berthelot) probably by the reaction—

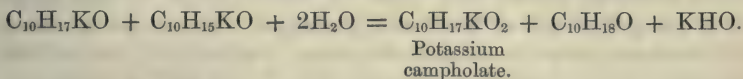


the nascent oxygen resinising part of the camphor. By the action of sodium on a solution of camphor in toluene, and of carbonic acid on the product, a much larger quantity of borneol is formed (Baubigny) by the reactions—



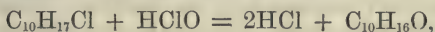


If potassium and a higher-boiling petroleum be employed, campholate of potassium and borneol are formed by the mutual reaction of potassium-borneol and potassium-camphor first formed, thus—

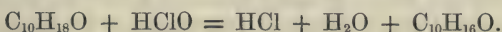


The natural borneol and that synthesized by the above two sets of reactions, exhibit respectively the rotatory powers,  $\alpha = + 33.4^\circ$ ,  $44.9^\circ$ , and  $42.4^\circ$ .

By the action of phosphorus pentachloride or of hydrochloric acid, borneol furnishes a chloride,  $\text{C}_{10}\text{H}_{17}\text{Cl}$ , melting at  $132^\circ$ ; this is converted into ordinary camphor by hypochlorous acid—



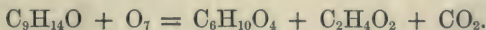
just as borneol is similarly converted into ordinary camphor—



Bromine acts on borneol, forming first camphor and hydrobromic acid, and finally a mixture of monobromocamphor and borneol bromide. Phosphoric anhydride acts on borneol, forming a hydrocarbon,  $\text{C}_{10}\text{H}_{16}$  (*borneene* of Pelouze), boiling at  $176^\circ$ — $180^\circ$ , and an isomeric condensation product distilling at  $250^\circ$ — $280^\circ$ ; borneene smells like turpentine, but does not unite with hydrochloric acid or with hypochlorous acid.

A number of substances of formula  $\text{C}_9\text{H}_{14}\text{O}$  have been described by different chemists as *camphrene* or *phorone*. The author gives a table of the principal properties and reactions exhibited by camphrene from camphor and by phorone: from (a) camphoric acid; (b) acetone by quicklime; (c) acetone and sodium; (d) grape sugar; (e) cane sugar; (f) acetone and hydrochloric acid; from which it would seem probable that the first five phorones are identical, while phorone (f) and camphrene are only isomeric with that substance.

Phorone prepared from camphoric acid, and boiling at  $206^\circ$ — $215^\circ$ , was boiled with chromic solution for two days in a flask, with upright condenser attached; on distillation with water, an acid distillate containing acetic acid was obtained. The residue was agitated with ether, which gave a syrupy extract, solidifying to a magma of crystals on standing a few days; this was converted into barium and silver salts, and proved to be *adipic acid*,  $\text{C}_6\text{H}_{10}\text{O}_4$ . Hence phorone splits up on oxidation, thus—



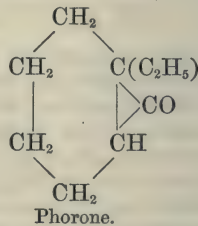
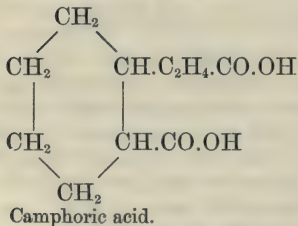
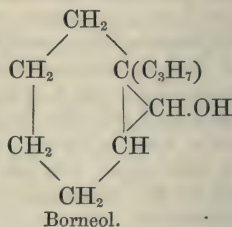
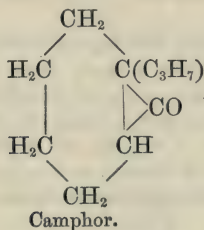
Camphrene prepared by Schwanert's process (*Ann. Chem. Pharm.*, cxxiii, 298) appears from the author's researches to be a mixture of phorone with a hydrocarbon, which raises its boiling point up to  $230^\circ$ — $235^\circ$ . On analysis an excess of carbon of 1 per cent. more than that indicated by the formula  $\text{C}_{10}\text{H}_{14}\text{O}$  was found, while the highest-boiling fraction contained only half the oxygen requisite for that formula; by oxidation with chromic liquor, acetic and adipic acids were formed, and also a small quantity of an acid of formula  $\text{C}_9\text{H}_8\text{O}_4$ ; apparently the camphrenic acid of Schwanert. On closer examination this substance appeared

to present all the properties of the insolinic acid of Hofmann (from cuminic acid); of the acid obtained by Hirzel and Beilstein from xyllylic acid by oxidation, and hence having the formula,  $C_6H_3(CH_3) \begin{Bmatrix} CO.OH \\ CO.OH \end{Bmatrix}$ ; and of the xylidic acid of Fittig and Laubinger. The author concludes that these are probably one and the same homologue of terephthalic acid, and that the so-called camphrenic acid of Schwanert is not an oxidation-product of phorone, but of the hydrocarbon with which the phorone is mixed in the so-called camphrene.

From the so-called camphrene, Schwanert obtained, by the action of phosphoric anhydride, a hydrocarbon  $C_9H_{12}$ , boiling at  $170^\circ$ — $175^\circ$ ; his analytical numbers, however, indicate that this was not free from oxygenised substances, and hence it cannot be concluded that this hydrocarbon was really distinct from the cumene (of boiling point  $150^\circ$ — $160^\circ$ ) derived from phorone. The statement that nitric acid only resinises phorone is not correct; when the action is pushed far enough, oxalic and adipic acids are formed, but no trace of insolinic acid.

The compound  $C_9H_{14}O$  obtained from acetone by hydrochloric acid (to which Baeyer ascribes the formula,  $\begin{matrix} CH_3 \\ \diagup \\ CH_3 \end{matrix} C \begin{matrix} CH_2 \\ \diagdown \\ CH_2 \end{matrix} C \begin{matrix} CH_2 \\ \diagdown \\ CH_2 \end{matrix} O$ , and Kekulé the formula,  $\begin{matrix} CH_3 \\ \diagup \\ CH_3 \end{matrix} C=CH-C(CH_3)=CH-CO-CH_3$ ) is certainly only isomeric with phorone, being a solid crystallisable body, boiling at  $196^\circ$ , and not yielding cumene with zinc chloride or phosphoric anhydride; whilst, on the other hand, the author considers all the other substances discussed in this paper to be identical (thus the product from cane-sugar obtained by Benedict, and found by him to yield acetic acid on oxidation, was found by the author also to yield adipic acid).

The author assigns the following formulæ to the undermentioned substances:—



C. R. A. W.

**On Phenylene-diacetic Acid.** By R. BILDERMANN (Deut. Chem. Ges. Ber., v, 702).

WHEN chlorine is passed into the vapour of boiling commercial xylene (a mixture of para-xylene and meta-xylene), a certain quantity of the body,  $\text{C}_6\text{H}_4 \begin{Bmatrix} \text{CH}_2\text{Cl} \\ \text{CH}_2\text{Cl} \end{Bmatrix}$  (obtained by Grimaux from synthetical methyl-toluene from solid bromo-toluene), is produced, and is obtainable by distilling till the boiling point reaches  $230^\circ$ , and bringing the tarry residue into a freezing mixture, when crystals of the compound are deposited; these are purified by crystallisation from alcohol. This substance melts at  $100^\circ$ , and exhibits all the properties assigned to it by Grimaux; it yields terephthalic acid by oxidation with chromic acid.

Bromine dropped into the vapour of the xylene through an upright condenser furnishes the corresponding dibromide,  $\text{C}_6\text{H}_4 \begin{Bmatrix} \text{CH}_2\text{Br} \\ \text{CH}_2\text{Br} \end{Bmatrix}$ , still more readily: all traces of moisture must be absent, otherwise decomposition sets in. On cooling, a magma of crystals is produced, from which the dibromide is obtainable by pressure and recrystallisation of the solid from alcohol. In all these operations the eyes are much attacked. The pure dibromide melts at  $143^\circ$  ( $145^\circ$ — $147^\circ$  Grimaux) and is readily soluble in boiling alcohol, difficultly in cold alcohol and ether.

On treating it with alcoholic potassium cyanide, the corresponding dicyanide,  $\text{C}_6\text{H}_4 \begin{Bmatrix} \text{CH}_2\text{CN} \\ \text{CH}_2\text{CN} \end{Bmatrix}$ , is produced (melting point  $88^\circ$ — $90^\circ$ ); an amorphous body, apparently a polymeride of this is also formed. On boiling the dicyanide with alcoholic potash ammonia is evolved, and *phenylene-diacetic acid*,  $\text{C}_6\text{H}_4 \begin{Bmatrix} \text{CH}_2\text{CO.OH} \\ \text{CH}_2\text{CO.OH} \end{Bmatrix}$  produced; this is precipitated in white flocks from the potash salt by acids; it is readily soluble in alcohol, less readily in ether. Hot water dissolves it readily, but in cold water it is almost insoluble. It cannot be obtained in a distinctly crystalline condition, and gives an amorphous silver salt; the calcium salt is, however, crystallisable.

Further researches to prepare the corresponding diamine, the diatomic mercaptan, &c., are contemplated.

C. R. A. W.

**Action of Potash on Benzoic Acid.** By L. BARTH (Ann. Chem. Pharm., clxiv, 138—150).

By fusing benzoic acid with caustic potash for half an hour to about  $360^\circ$ , paraoxybenzoic acid is formed, together with a yellow amorphous acid, having the composition  $\text{C}_{10}\text{H}_{14}\text{O}_3$ , and brown resinous bodies. Besides these substances, a small quantity of an acid,  $\text{C}_{14}\text{H}_{12}\text{O}_7$ , is produced, which is also formed when paraoxybenzoic acid is fused with caustic potash. It crystallises from dilute alcohol in microscopic prisms, is readily soluble in alcohol and ether, and gives with ferric chloride a violet-red colour. The most remarkable of these results is the formation of paraoxybenzoic acid, which is produced by the direct oxidation of benzoic acid.

C. S.



**On Bromochlorosalicylic and Bromochlorobenzoic Acids.** By AD. CLAUS and Dr. PFEIFER (Deut. Chem. Ges. Ber., v, 656—659).

THE three chlorobenzoic acids are not all converted with equal ease into the corresponding bromochlorobenzoic acids by the action of bromine on their aqueous, alcoholic, or ethereal solutions. Chlorosalicylic acid is scarcely altered even after heating with bromine in sealed tubes, whereas chlorobenzoic acid is acted upon with comparative readiness. They may all be easily brominated, however, by the action of bromine on a hot solution of the silver salt.

*Bromochlorosalicylic acid* crystallises in fine, small, glistening needles, melting at  $151^{\circ}$ , and soluble in 380 parts of water at  $21^{\circ}$  C. Like chlorosalicylic acid, it melts under boiling water, but is more soluble than that acid. Its salts are also more soluble than the corresponding chlorosalylates. The potassium, calcium, and barium salts were prepared.

*Bromochlorobenzoic acid* also crystallises in fine, white, felted needles, but is less soluble than the above (1080 parts of water at  $21^{\circ}$  dissolve 1 part of the acid) and does not melt under boiling water. Its barium salt crystallises with two molecules of water; that of the above-mentioned isomeric acid contains three.

In the preparation of chlorobenzoic acid by the action of potassium chlorate and hydrochloric acid on benzoic acid, it was found that no inconsiderable quantities of dichlorobenzoic acid were formed. The properties of the acid thus obtained differ in several respects from those described as characteristic of dichlorobenzoic acid by Otto, and by Beilstein and Kuhlberg.

Experiments are in progress to convert the above acids into dioxybenzoic acids by fusion with potassium hydrate. This appears to succeed if the temperature be carefully regulated, but if the heating be carried too far, chlorobromo salylic acid yields considerable quantities of salicylic acid.

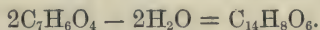
H. E. A.

**Derivatives of Dioxybenzoic Acid.** By L. BARTH and C. SENHOFER (Ann. Chem. Pharm. clxiv, 109—126).

By the destructive distillation of dioxybenzoic acid a yellow crystalline body is obtained, and the same substance is formed when this acid is heated for an hour with four times its weight of sulphuric acid to  $120^{\circ}$ — $140^{\circ}$ . On adding water to the dark blood-red solution the new compound separates as a dark-green powder, which may be purified by dissolving it in alcohol and boiling the solution with animal charcoal. From the yellow filtrate the substance is precipitated by the addition of water in crystalline flakes, having the composition  $C_{14}H_8O_6 + 2H_2O$ , and becoming anhydrous when dried at  $100^{\circ}$ . This body is not an anhydride of dioxybenzoic acid, as by heating it with water or potash it is, according to the temperature, either not altered at all or completely destroyed.

By heating it with zinc-dust it is reduced to anthracene; it is therefore a tetraoxyanthraquinone, and its formation is quite analogous

to that of rufigallic acid from gallic acid and that of rufiopin from opianic acid—



*Anthrachryson*, as the authors call this compound, forms a golden-yellow crystalline powder, which, when heated, gives off a quinone-like smell, but does not melt even at  $320^\circ$ . It can be distilled without decomposition, and is but sparingly soluble in alcohol and less so in benzene and toluene. Water dissolves only traces; in dilute sulphuric acid or hydrochloric acid and carbon bisulphide it is quite insoluble. The best solvent for it is glacial acetic acid; water precipitates it from this solution in greenish-yellow flakes. Although possessing the characteristic properties of a quinone, anthrachryson is not acted upon by sodium-amalgam.

On heating it with a large quantity of water and freshly-precipitated barium carbonate, the compound  $(C_{14}H_7O_6)_2Ba + 11H_2O$  separates on standing in dark-red crystalline flakes. The same salt is obtained in needles half an inch long when anthrachryson is heated with the right quantity of baryta-water and the solution is concentrated. On adding barium chloride to a solution of the ammonium salt, dark-red needles, having the composition  $C_{14}H_6O_6Ba$  gradually crystallise out. When calcium chloride is added to the ammoniacal solution, the calcium salt is obtained as a precipitate consisting of light-red microscopic needles. The magnesium and aluminium salts are amorphous red precipitates; the copper- and silver-salts, brown amorphous masses. By fusing anthrachryson with potash, a large quantity of a humus-like substance is formed, together with a small quantity of a crystalline body. Anthrachryson dyes on iron-mordants a brown colour, and on alumina-mordants it produces a colour like that of alizarin, but duller.

*Monobromodioxybenzoic acid*,  $C_7H_5BrO_4$ , is produced by adding a sufficient quantity of bromine-water to a cold aqueous solution of the acid. On evaporating the solution and crystallising the residue from hot water, monobromodioxybenzoic acid is obtained in colourless needles an inch long, melting at  $253^\circ$ . Its solution gives a brownish precipitate with ferric chloride, but it is not precipitated by lead acetate. The crystallised acid contains one molecule of water, which it loses at  $120^\circ$ . By heating it with sulphuric acid it is converted into anthrachryson.  $C_7H_2Ag_3BrO_4$  is a yellow amorphous precipitate obtained by adding silver nitrate to the ammonium salt. The baryta salt is readily soluble in water and crystallises in long needles. The copper salt separates from a hot solution in light-green microscopic but well-defined prisms  $(C_7H_4BrO_4)_2Cu + 8H_2O$ . The potassium salt crystallises in needles and dissolves very readily in water.

By fusing the monobrominated acid with potash, a large quantity is converted into dioxybenzoic acid and a smaller quantity into gallic acid.

When tribromodioxybenzoic acid is fused with potash, nearly the whole is reconverted into dioxybenzoic acid; there is also formed a small quantity of a compound which gives a green colour with ferric chloride.

*Diethyldioxybenzoic acid*,  $C_7H_4O_4(C_2H_5)_2$ , is produced by heating the ethyl-ether with ethyl iodide, caustic potash, and a little alcohol in



sealed tubes to  $130^{\circ}$  for some hours. The ethylic diethyl-dioxybenzoate thus formed is an oily liquid which is readily decomposed by boiling it with potash. The free acid crystallises from water in needle-shaped prisms, melting at  $87^{\circ}$ — $88^{\circ}$ . The barium salt has the composition  $(C_{11}H_{13}O_4)_2Ba$ . By heating diethyl-dioxybenzoic acid with quicklime, an oil is obtained boiling between  $200^{\circ}$ — $260^{\circ}$ , containing probably the diethyl-ether of resorcin. The latter compound is easily obtained by heating resorcin with ethyl iodide and potash; it is an oily liquid boiling at  $250^{\circ}$  and giving no colour with ferric chloride. By heating it with hydriodic acid it is not reconverted into resorcin, but a resinous body is produced, the alkaline solution of which exhibits, even when very dilute, a strong dichroism, appearing green in reflected light and yellowish-red by transmitted light. Exactly the same reaction is shown by the distillate of a mixture of diethyl-dioxybenzoic acid and lime.

As the disulphobenzoic acid from which the dioxybenzoic acid is obtained yields isophthalic acid when it is fused with sodium formate, and as further the dioxy-acid seems to yield resorcin, it appears most probable that the side chains in these acids have the positions 1, 3, 6.

C. S.

**Sulpho-acids of Benzene.** By H. ROSE (*Zeitschr. f. Chem.* [2], vii, 234).

PURE nitro-benzene was dissolved in about its own volume of sulphuric acid, and the solution was kept for some weeks in a warm place. The barium salt, which has already been obtained by Schmitt (*Ann. Chem. Pharm.*, cxx, 163), was then prepared, and from it the free acid, which was found to crystallise in leaf-like masses, efflorescing over sulphuric acid and deliquescing in damp air. It melts between  $60^{\circ}$  and  $70^{\circ}$ , and though very soluble in alcohol it is almost insoluble in ether. Both the acid and its salts are intensely bitter. *Barium salt*,  $(C_6H_4.NO_2SO_3)_2Ba + H_2O$ : small, slightly yellow, hard crystals, easily soluble in hot water but almost insoluble in alcohol. *Lead salt*,  $(C_6H_4.NO_2SO_3)_2Pb + 2H_2O$ : large, white nodules, very soluble in hot water and tolerably soluble in cold water and alcohol. It is precipitated from its alcoholic solution by ether. *Calcium salt*, very soluble in hot water and tolerably soluble in alcohol, from which it is precipitated by ether. When obtained by the rapid cooling of a concentrated solution, it forms shining leaflets  $(C_6H_4.NO_2SO_3)_2Ca + 3H_2O$ ; but from a less concentrated solution it separates by slower cooling in large clear prisms  $(C_6H_4.NO_2SO_3)_2Ca + 2H_2O$ . *Copper salt*,  $(C_6H_4.NO_2SO_3)_2Cu + 4H_2O$ : light green prisms, very soluble in water and easily soluble in alcohol. *Potassium salt*,  $C_6H_4.NO_2SO_3K$ : shining leaflets from hot concentrated solution, long needles from dilute solution. It is easily soluble in hot water and slightly soluble in alcohol, from which it is precipitated by ether. *Sodium salt*: small leaflets, very soluble in hot alcohol and water. The alcoholic solution to which ether has been added deposits the salt in fine crystals.

The author is engaged in the further study of this acid and its amido-acid, which has been already obtained by Schmitt. He also



intends to compare it with the product of the nitration of benzenesulphonic acid, and its amido-acid with that of the last-named acid.

T. B.

**Benzylsulphonic Acid.** By G. A. BARBAGLIA (Deut. Chem. Ges. Ber., v, 687—689).

THIS acid has already been examined by the author who obtained it by the action of potassium sulphite on benzyl chloride. From its reactions the author concluded that the group  $\text{SO}_3\text{H}$  was linked to the carbon by oxygen. It appeared therefore of interest to compare this acid with that obtained by the oxidation of the sulphides of benzyl. Benzylhydrosulphide was converted into the bisulphide by adding bromine to its ethereal solution, and the product was oxidised with nitric acid of different strengths. The result was the formation of much benzaldehyde, a little benzoic acid, and benzylsulphonic acid, identical with that obtained before.

As this method yields the body in small quantities only, the oxidation of benzyl sulphocyanate was next tried. This compound was obtained by heating benzyl chloride with an alcoholic solution of potassium sulphocyanate. It crystallises from alcohol or ether in prisms melting at  $41^\circ$ , and boiling at  $230^\circ$ — $235^\circ$ . On oxidising it with nitric acid it yields only benzaldehyde and benzoic acid, but no sulpho-acid.

C. S.

**Toluene-disulphonic Acid and some of its Derivatives.** By C. SENHOFER (Ann. Chem. Pharm., clxiv, 126—138).

THIS acid is obtained by heating toluene with Nordhausen sulphuric acid and phosphorus pentoxide for four or five hours to  $2300^\circ$ . On opening the tubes, a large quantity of sulphur dioxide is evolved. The brown residue is dissolved in water, and the solution is boiled and neutralized with barium carbonate. By adding alcohol to the concentrated filtrate the barium salt is obtained as a white precipitate, having the composition  $\text{C}_6\text{H}_3(\text{CH}_3)(\text{SO}_3)_2\text{Ba} + 3\frac{1}{2}\text{H}_2\text{O}$ . The potassium salt is prepared by adding milk of lime to a solution of the crude acid and precipitating the calcium salt with potassium carbonate. Purified by recrystallisation, it forms short, well-defined prisms, of the composition  $\text{CH}(\text{CH}_3)(\text{SO}_3)_2\text{K}_2 + \text{H}_2\text{O}$ .

By decomposing the barium salt with sulphuric acid, evaporating the filtrate, and exhausting the residue with a mixture of alcohol and ether a solution of the free acid is obtained, crystallising *in vacuo* over sulphuric acid in soft microscopic needles, which could not be obtained quite pure.

The silver-salt,  $\text{C}_6\text{H}_3(\text{CH}_3)(\text{SO}_3\text{Ag})_2 + 2\text{H}_2\text{O}$ , is obtained by neutralizing a boiling solution of the acid with silver-oxide; it forms yellow crystals. The cadmium salt is a gum-like mass, and the ammonium salt forms very soluble needles.

By fusing the potassium salt with potash, salicylic acid and *isorcin*,  $\text{C}_7\text{H}_5\text{O}_2$ , are produced. The latter compound melts at  $87^\circ$ , boils at  $260^\circ$ , and solidifies on cooling to a radiate crystalline mass. It has a

faint, sweet taste and dissolves in water, alcohol, and ether. Isorcin has great resemblance to orcin, from which it, however, it differs by its reactions. Its solution does not assume a red colour when exposed to the air; with ferric chloride it yields a brownish-green colour; it reduces ammonical silver solutions even in the cold, and gives with bleaching powder a red colour, changing gradually into yellow. In presence of ammonia and air, it acquires a brown colour, but becomes colourless again on the addition of acetic acid.

When potassium toluenedisulphonate is fused with sodium formate, it is converted into the potassium salt of *isoxylidic acid*,  $C_6H_3(CH_3)(CO_2H)_2$ . This acid is almost insoluble in cold water, sparingly soluble in hot water, but readily in alcohol and ether, and forms microscopic crystals. When heated it begins to soften at  $280^\circ$ , but does not melt completely till heated to  $375^\circ$ . By sublimation it is obtained in yellowish, well-defined needles. The barium salt,  $C_6H_3(CH_3)(CO_2)_2Ba + 2H_2O$ , is a yellowish, crystalline mass; the silver-, lead-, cadmium-, and copper-salts are amorphous precipitates.

C. S.

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**Sulphopara-oxybenzoic Acid.** By R. KOELLE (Ann. Chem. Pharm., clxiv, 150—154).

THIS acid is produced by acting with the vapour of sulphuric anhydride on dry paro-oxybenzoic acid; a syrupy, brown mass is thereby formed, which is to be diluted with water and neutralized with quick lime. The solution of the calcium salt is precipitated with potassium carbonate, and lead acetate is added to the filtrate. The bulky precipitate, which is insoluble in water, is decomposed by hydrogen sulphide and the solution of the free acid evaporated on a water-bath. The crude acid thus obtained is purified by dissolving it in absolute alcohol, evaporating the solution, and recrystallising the residue from water. The acid is very soluble in water and alcohol, crystallises in deliquescent, white, silky needles, and gives a blood-red colour with ferric chloride.

On evaporating a solution of the potassium salt, first quadratic plates, having the composition  $C_7H_3K_3SO_6 + 2H_2O$ , crystallise out, and from the mother-liquor the salt,  $C_7H_4K_2SO_6 + H_2O$ , is obtained in needles. That both salts contain the same acid is shown by the fact that the latter salt, by addition of caustic potash, may be converted into the quadratic salt, and that both, when fused with caustic potash, yield protocatechuic acid.

The neutral barium salt,  $2(C_7H_4BaSO_6) + 7H_2O$ , crystallises from water in small plates, and the basic salt,  $(C_7H_3SO_6)_2Ba$ , is obtained as an amorphous powder by adding barium chloride to a solution of the basic potassium salt. The silver-salt,  $C_7H_4Ag_2SO_6$ , separates from a hot aqueous solution in crystalline flakes. The copper-salt,  $C_7H_4CuSO_6$ , remains on evaporating its solution, as a dark-green amorphous powder; the cadmium salt,  $C_7H_4CdSO_6 + 3H_2O$ , forms microscopic crystals and is readily soluble in water.

C. S.

**Mesitylene-sulphonic Acids.** By HEINRICH ROSE (Ann. Chem. Pharm., clxiv, 53—74).

THE object of the investigation was to ascertain whether isomeric substituted sulpho-acids of mesitylene could be prepared, the formation of such isomerides being impossible according to present views, since the three methyl groups in mesitylene are regarded as occupying symmetrical positions.

*Mesitylenesulphonic acid*,  $C_6H_2(CH_3)_3SO_3H$ .—The action of sulphuric acid gives rise to the formation of only one acid of this composition, according to the author. The preparation of the acid, and of its barium, lead, and magnesium salts, is described at length. It was converted into *monobromomesitylene-sulphonic acid* by the action of bromine on an aqueous solution; the yield, however, is extremely small, the main product consisting of brominated mesitylenes. The barium, lead, potassium, sodium, copper, and calcium salts of the brominated acid are fully described. An acid of the same composition, and *identical properties*, was obtained by the action of fuming sulphuric acid on monobromomesitylene, but even in this case the yield is not very satisfactory.

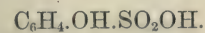
*Nitromesitylenesulphonic acid*.—Mesitylene-sulphonic acid is violently acted upon by fuming nitric acid, and converted into nitromesitylenes; by careful nitration, however, it yields a mononitro-derivative, of which the barium, potassium, lead, and copper salts were prepared. It is converted by reduction with ammonium sulphide into *amidomesitylenesulphonic acid*, a well crystallised compound, yielding a series of well-defined salts. Nitromesitylene is soluble in fuming sulphuric acid, but is reprecipitated on addition of water.

H. E. A.

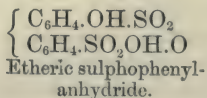
**Synthesis of Sulphotannic Acids.** By HUGO SCHIFF (Deut. Chem. Ges. Ber., v, 661—664).

THIS communication refers to the production of a new class of bodies, the etheric anhydrides of the aromatic sulphonic acids, which exhibit in a remarkable manner the characteristic behaviour of tannic acid. They are obtained by the action of phosphorus oxychloride on the sulphonic acids.

Phenolsulphonic acid thus treated yields a product which is readily soluble in water, but is almost entirely reprecipitated on the addition of hydrochloric acid. In the pure state it is a white, mealy powder having the composition,  $C_{12}H_{10}S_2O_7$ . It is a monobasic acid; is converted into a monacetyl derivative by the action of acetic anhydride; yields a pale, violet coloration with ferric chloride, and may therefore be formulated thus:—



Phenolsulphonic acid.



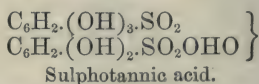
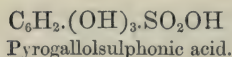
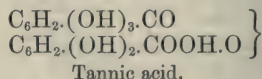
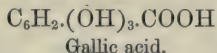
Etheric sulphophenyl-anhydride.

This compound is in every respect a true tannic acid.

*Sulphotannic Acid*.—Pyrogallol was converted into sulpho-acid by the action of pure pyrosulphuric acid prepared by dissolving one mole-



cule of sulphuric anhydride in one molecule of sulphuric acid. On treating the acid,  $C_6H_2.(OH)_3.SO_2OH$ , thus obtained, with phosphorus oxychloride, it is converted into the corresponding etheric-anhydride, which may be precipitated from an aqueous solution by hydrochloric acid in white flocculi. This anhydride bears the same relation to pyrogallolsulphonic acid that tannic acid bears to gallic acid:—

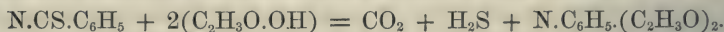


In properties it also resembles tannic acid most closely.

H. E. A.

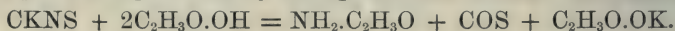
### New Method of Preparing Amides and Nitriles. By E. A. LETTS (Dent. Chem. Ges. Ber., v, 669—674).

It had been shown by Hofmann that phenyl isosulphocyanate is converted by heating with acetic acid into phenyl-diacetamide:—



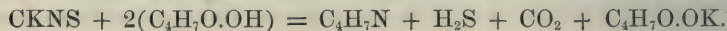
It became therefore a question what would be the behaviour of the metallic sulphocyanates under similar conditions.

*Acetic Acid and Potassium Sulphocyanate.*—The latter dissolves readily in boiling acetic acid, and gas is at once evolved, but long continued heating is required to complete the reaction, which in the main takes place as represented by the equation:—



At the same time, however, acetonitrile, carbonic anhydride, and hydrogen sulphide are formed in small quantity in virtue of a secondary reaction.

*Isobutyric Acid and Potassium Sulphocyanate.*—Reaction is sooner completed in this case, owing to the higher boiling point of the acid employed. The main products are carbonic oxysulphide and isobutyramide. The latter is a white crystalline substance, of pleasant aromatic odour, melting at  $100^\circ$ — $102^\circ$ , and boiling at  $216^\circ$ — $220^\circ$ ; 200 grams of acid gave 60 grams of the pure amide. Isobutyronitrile, carbonic anhydride, and hydrogen sulphide—product of the secondary reaction,



are also obtained.

The reaction between *valeric acid* and potassium sulphocyanate is perfectly analogous, and yields valeramide, valeronitrile, carbonic oxysulphide and anhydride, and hydrogen sulphide.

In the case of the aromatic acids, almost the entire product consists of the nitrile. Thus *benzoic acid* gave benzonitrile:—



Cuminic acid gave cumonitrile. No satisfactory result was obtained with cinnamic acid. No less than 80 per cent. of the calculated quantity of benzonitrile may be obtained by this process. The mixture in the above proportions is placed in a flask, and heated either in a paraffin bath, or over the bare flame. The substances melt and form two layers, reaction commences at 190°, and the contents of the flask begin to boil at a somewhat higher temperature, but after about half an hour the whole solidifies to a white mass. The vessel is then strongly heated, and the distillation continued as long as possible, avoiding carbonisation of the residue, which consists of potassium benzoate. The semi-solid distillate is a mixture of benzoic acid and benzonitrile, from which the former may be separated by shaking with ammonia, &c.

H. E. A.

**Allyl Cyanide or Crotonitrile.** By RINNE and TOLLENS (Zeitschr. f. Chem. [2], vii, 251).

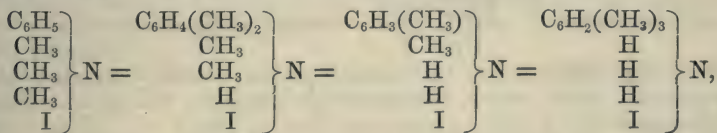
By heating pure allyl iodide with pure pulverised potassium cyanide to 110° for two days, washing the product, again heating with potassium cyanide, and fractionating after treatment with a few drops of nitric acid, the authors succeeded in obtaining allyl cyanide in a state of purity. It boils at 116°–118°, has a not disagreeable, alliaceous odour, and is converted by alcoholic or aqueous potash into crotonic acid, melting at 71°–72°. This allyl cyanide is therefore identical with that of Will and Körner, and the crotonic acid with that of the same investigators.

The penetrating odour of the portion of the crude allyl cyanide boiling from 90° to 100°, indicates the presence of Lieke's allyl cyanide.

T. B.

**Synthesis of Aromatic Monamines by the moving about of Atoms in a Molecule.** By A. W. HOFMANN (Deut. Chem. Ges. Ber., v, 704).

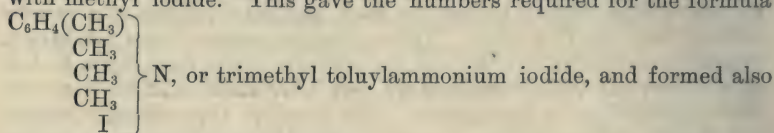
WHEN trimethylphenylammonium iodide (prepared from pure dimethyl aniline and methyl iodide) is heated in a sealed tube to 200°, no change takes place; but if it be heated for a day to 220°–230, or to higher temperatures, changes ensue, expressed by the equations—



*i.e.*, there is first formed the hydriodide of the tertiary base, *dimethyl-toluidine*; then the hydriodide of the secondary base, *methyl-dimethyl-phenylamine*, or *methyl-xyloidine*; and finally the hydriodide of the primary base, *trimethylphenylamine*, or *cumidine*.

The products formed at 220°–230° when decomposed by alkali yielded an oily mixture of bases boiling between 200° and 280°. The

lowest boiling fraction finally obtained boiled at  $186^{\circ}$ , gave a platinum salt and analytical numbers agreeing with those required for dimethyl toluidine, and produced a quaternary iodide on treatment with methyl iodide. This gave the numbers required for the formula

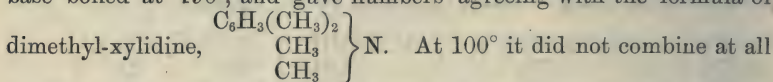


the corresponding platinum salt.

The higher boiling portions could not be separated completely by fractional distillation. Portions collected at the temperatures  $200^{\circ}$ — $203^{\circ}$ ,  $203^{\circ}$ — $208^{\circ}$ ,  $208^{\circ}$ — $212^{\circ}$ ,  $212^{\circ}$ — $220^{\circ}$ , were treated with methyl iodide, whereby crystalline solid products were obtained, which all had the composition *trimethyltoluylammonium iodide*, and yielded the corresponding platinum salt. These iodides were mixed together, decomposed by silver hydrate, and the resulting hydrates decomposed by distillation. A tertiary base was thus produced, boiling constantly at  $205^{\circ}$ , and having the same composition as the dimethyl-toluidine boiling at  $186^{\circ}$ . Hence *two isomeric dimethylized toluidines are formed by the action of heat on trimethylphenylammonium iodide*.

In order to decide whether either of these corresponds to the dimethylized toluidine obtained by methylizing solid toluidine, some of this latter was prepared from pure solid toluidine by the action of methyl iodide, and was found to boil at  $207^{\circ}$ — $208^{\circ}$ . This was converted into trimethyltoluylammonium iodide, which was decomposed by silver iodide and distillation, furnishing a pure dimethyl toluidine boiling constantly at  $210^{\circ}$ . This base resembled in smell the former one boiling at  $205^{\circ}$ , but differed from the one boiling at  $186^{\circ}$ . It is thus not improbable that *three* dimethyl-toluidines have been obtained; but until the dimethylized bases corresponding to the other two toluidines have been investigated, it cannot be said with certainty that the bases boiling at  $205^{\circ}$  and  $210^{\circ}$  are really isomeric. All three dimethylized toluidines remained liquid when cooled to  $-10^{\circ}$ .

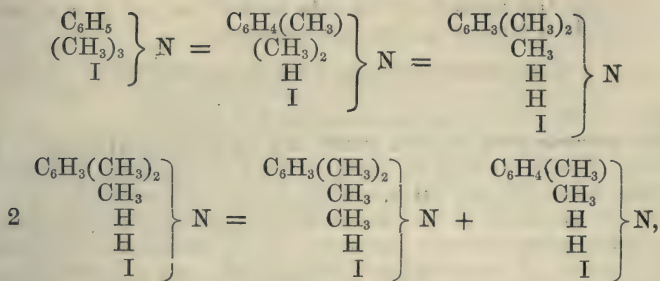
The above-mentioned fractions between  $203^{\circ}$  and  $220^{\circ}$  yielded, on treatment with methyl iodide in excess, not only the crystalline trimethyl-toluylammonium iodide, but also a small quantity of a base which only combined with methyl iodide with great difficulty. This base boiled at  $196^{\circ}$ , and gave numbers agreeing with the formula of



with methyl iodide, but at  $150^{\circ}$  a small portion became converted into a quaternary iodide, which furnished the platinum salt of *trimethyl-xylylammonium*.

This dimethyl-xylylidine is probably formed by the alteration by a secondary reaction of the hydriodide of methyl-xylylidine produced by the isomeric conversion of the original trimethylphenylammonium iodide, probably thus:—





so that monomethyl-toluidine and dimethyl-xylidine are complementary products.

Dimethyl-xylidine was prepared for comparison from xylidine of boiling point  $216^\circ$ , contained in commercial aniline, by treatment with methyl iodide. This variety boiled at  $203^\circ$ , or  $7^\circ$  higher than that from trimethylphenylammonium iodide, and readily united with methyl iodide to form a quaternary iodide.

When the isomeric transformation of trimethylphenylammonium iodide was effected at a temperature of about  $335^\circ$  (melting point of lead), a further action was noticed, and also the production of several bye-products by secondary reactions. On distilling with water the acid product of the action, a considerable quantity of hydrocarbons, partly solid partly fluid, was obtained. When the residue was distilled with caustic soda, a mixture of bases distilled, the principal portion of which boiled at  $217^\circ$ — $230^\circ$ , and furnished a crystalline hydrochloride, from which was isolated a base boiling constantly at  $225^\circ$ — $227^\circ$ . This was a *cumidine*,  $\left. \begin{array}{c} \text{C}_6\text{H}_2(\text{CH}_3)_3 \\ \text{H}_2 \end{array} \right\} \text{N}$ , which was shown to be a primary

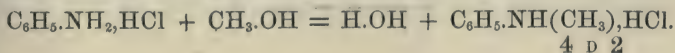
base by methylation. The dimethyl cumidine thus obtained boiled at  $213^\circ$ — $214^\circ$ , and absolutely refused to combine with methyl iodide to form a trimethylecumylammonium iodide. The dimethyl-cumidine and dimethyl-xylidine obtained in the manufacture of dimethyl-aniline, on the other hand, readily unite with methyl iodide, forming quaternary compounds. The cumidine thus obtained from aniline did not yield a trace of colour by the action of corrosive sublimate; but when a mixture of this cumidine and pure aniline was similarly treated, a beautiful carmine-red colouring matter resulted.

A large number of questions are suggested by the foregoing experiments. The author proposes to examine in detail a number of points thus suggested.

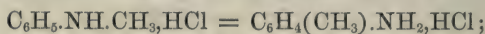
C. R. A. W.

### Conversion of Aniline into Toluidine. By A. W. HOFMANN (Deut. Chem. Ges. Ber., v, 720).

WHEN pure aniline hydrochloride is heated to  $230^\circ$ — $250^\circ$  for several hours with methyl alcohol, a yellow transparent honey-like mass is obtained, consisting chiefly of *methylaniline hydrochloride*:



On heating the contents of the tube to  $350^{\circ}$  for a day, a crystalline hydrochloride is formed by the transformation



in short, *methylaniline becomes converted into toluidine*.

After recrystallisation from water, this toluidine melts at  $45^{\circ}$ ; when, however, the hydriodide of methylaniline is similarly treated, solid toluidine is not formed, but one of the liquid modifications.

The bye-products of the action of heat (about  $330^{\circ}$ ) on trimethylphenylammonium contain, amongst other substances, a crystalline primary amine of constitution  $\text{C}_6(\text{CH}_3)_5\cdot\text{NH}_2$ , and a beautifully crystallised hydrocarbon melting at  $136^{\circ}$  and boiling at  $230^{\circ}$ — $240^{\circ}$ , which gives numbers agreeing with the formula  $\text{C}_6(\text{CH}_3)_6 =$  *hexmethylated benzene*.

C. R. A. W.

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**Action of Ammonia on Nitranisic Acid and the Phenylene-diamine of Griess.** By H. SALKOWSKI (Deut. Chem. Ges. Ber., v, 722).

WHEN nitranisic acid is heated to  $160^{\circ}$  with ammonia, the group  $\text{OCH}_3$  is replaced by  $\text{NH}_2$ , and a *nitroparamidobenzoic acid* results, the formula of which is either 1 : 2 : 4 or 1 : 3 : 4, the  $\text{CO}_2\text{H}$  group being in position 1, and the  $\text{NH}_2$  group in position 4.

By reducing the  $\text{NO}_2$  group to  $\text{NH}_2$ , there is obtained a *diamidobenzoic acid*, which furnishes by dry distillation a *diamidobenzene* (i.e., a *phenylene-diamine*) identical with that obtained from Griess's  $\beta$ -diamidobenzoic acid, melting at  $99^{\circ}$  and boiling at above  $250^{\circ}$  (Griess gives  $99^{\circ}$  and  $252^{\circ}$  respectively).

By acting on this nitroparamidobenzoic acid with cold alcoholic nitrous acid, a diazo-compound results, from which a *nitrobenzoic acid* is obtained by boiling with absolute alcohol. The diazo body has the

formula  $\text{C}_6\text{H}_3(\text{NO}_2) \left\{ \begin{array}{l} \text{N}=\text{N} \\ \text{CO} \end{array} \right\} \text{O}$ . The nitrobenzoic acid appears to be

the ordinary (ortho) nitrobenzoic acid, as it melts at  $140^{\circ}$ — $141^{\circ}$ , and forms an ether melting at  $40^{\circ}$ — $41^{\circ}$ , an amide melting at  $140^{\circ}$  and an amidobenzoic acid (by reduction with zinc and hydrochloric acid) melting at  $172^{\circ}$ .

Hence it follows that ordinary nitrobenzoic acid and the corresponding substances of the same rank (viz., amido-, oxy-, benzoic acids, &c.), have not the same side-chain relations as Griess's phenylene-diamine. If the former are 1 : 3, as is most probable, the latter must be 1 : 2. Meyer finds that this phenylenediamine does not give any quinone odour on oxidation; but the author finds that a powerful smell of quinone is developed by treating it with potassium chromate and sulphuric acid, and hence concludes that this is another instance showing that the production of quinone by oxidation does not enable us to draw any conclusion as to the constitution of a benzene derivative.

C. R. A. W.

**Secondary Monamines of the Aromatic Series.** By C. GIRARD and G. VOGT (Bull. Soc. Chim. [2], xviii, 67—69).

THE authors have prepared a number of these bases in the pure state by the method of Girard and de Laire. This consists in heating to 280°—300° in a closed vessel for 30 hours a primary monamine with the hydrochloride of another primary monamine, and purifying the resulting secondary monamine.

*Phenyl-naphthylamine*,  $\left. \begin{matrix} \text{C}_6\text{H}_5 \\ \text{C}_{10}\text{H}_7 \\ \text{H} \end{matrix} \right\} \text{N}$ , is solid at ordinary temperatures,

slightly yellowish, after a time red; melts at 58°; distils at 335° (528 mm. bar.) and 226° (15 mm. bar.). It gives a greenish colour turning to red with a mixture of sulphuric and nitric acids.

*Cresyl-naphthylamine*,  $\left. \begin{matrix} \text{C}_7\text{H}_7 \\ \text{C}_{10}\text{H}_7 \\ \text{H} \end{matrix} \right\} \text{N}$ , occurs as a confused mass of

colourless crystals which gradually become red; melts at 78°; boils at about 360° (528 mm. bar.) and at 236° (15 mm. bar.). With a mixture of nitric and sulphuric acids it turns brown, then green, and finally brown.

*Xyl-yl-naphthylamine*,  $\left. \begin{matrix} \text{C}_8\text{H}_9 \\ \text{C}_{10}\text{H}_7 \\ \text{H} \end{matrix} \right\} \text{N}$ , has not been obtained solid, but in

the form of a viscous liquid, rapidly becoming brown, and boiling at 243°—245° (15 mm. bar.). It is no doubt a mixture of isomeric bodies arising from the isomeric xylenes contained in the hydrocarbon boiling at 139°.

*Dinaphthylamine*,  $\left. \begin{matrix} \text{C}_{10}\text{H}_7 \\ \text{C}_{10}\text{H}_7 \\ \text{H} \end{matrix} \right\} \text{N}$ , occurs in crystals apparently square,

with truncated edges. It melts at 113°, and boils at about 310°—315° (15 mm. bar.).

*Phenyl-xylylidine*,  $\left. \begin{matrix} \text{C}_6\text{H}_5 \\ \text{C}_8\text{H}_9 \\ \text{H} \end{matrix} \right\} \text{N}$ , is solid, and, after fusion, crystalline.

Like the preceding bodies, it is soluble in alcohol, benzene, ether, and the light rock-oils. The hydrochloride of this and of all the others of this series can only be obtained in anhydrous liquids; they are best prepared by passing hydrochloric acid into a benzene solution of the base. Phenylxylylidine boils at 278°—282° (485 mm. bar.) and at 173° (15 mm. bar.); it melts at 52°.

*Cresyl-xylylidine*,  $\left. \begin{matrix} \text{C}_7\text{H}_7 \\ \text{C}_8\text{H}_9 \\ \text{H} \end{matrix} \right\} \text{N}$ , is solid and readily crystallisable, either by

solution or fusion. From solution it separates in long, white, silky, light needles, like those of quinine sulphate; after fusion it takes the form of elongated plates, which gradually become coloured. It melts at 70°, and boils *in vacuo* at 194°, and at 298°—302° (487 mm. bar.).



*Diisylidine*,  $\left. \begin{matrix} \text{C}_6\text{H}_9 \\ \text{C}_6\text{H}_9 \\ \text{H} \end{matrix} \right\} \text{N}$ . There are two of these bodies, one solid, the

other liquid. They boil at about  $305^\circ$ — $315^\circ$ , and *in vacuo* at about  $205^\circ$ . The solid body occurs under the form of silky, matted crystals, which melt at  $162^\circ$ .

*Dicresylamine* has been elsewhere partly described; its melting point is  $145^\circ$ . E. D.

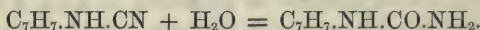
**Derivatives of Benzylamine.** By J. STRAKOSCH (Deut. Chem. Ges. Ber., v, 692—699).

THE derivatives of benzylamine have been but little studied, owing to the difficulty of obtaining this base in sufficient quantity. This difficulty does not longer exist, since Letts has prepared the cyanate and cyanurate of benzyl, and these ethers are readily converted into benzylamine by Wurtz's method. The product obtained by heating benzyl chloride with silver cyanate is distilled and the distillate, consisting of a mixture of the cyanate and cyanurate, is digested with caustic potash and subjected to distillation. The product generally contains some di- and tri-benzylamine owing to the presence of some undecomposed benzyl chloride. To purify it the distillate is treated with hot hydrochloric acid; tribenzylamine hydrochloride then remains undissolved, while the salt of dibenzylamine soon crystallises out. The solution is then decomposed by caustic potash, and the base dried over solid potash; it boils constantly at  $185^\circ$ .

*Cyanbenzylamine*,  $(\text{C}_7\text{H}_7.\text{NH}_2)_2(\text{CN})_2$ , is produced by passing cyanogen-gas into a cold solution of benzylamine; recrystallised from alcohol it forms colourless, shining crystals melting at  $140^\circ$ . It is insoluble in water, but dissolves in alcohol and ether. The hydrochloride  $(\text{C}_7\text{H}_7.\text{NH}_2)_2(\text{CN})_2.2\text{HCl}$ , crystallises in white silky needles; it is soluble in water and alcohol, and forms a crystalline platinum-compound. When cyanbenzylamine is heated for some time with hydrochloric acid, it is converted into benzyloxamide, dibenzyloxamide, and, on continued heating, even into oxamide.

*Dibenzyloxamide*,  $\left. \begin{matrix} \text{CO.N}(\text{C}_7\text{H}_7)\text{H} \\ \text{CO.N}(\text{C}_7\text{H}_7)\text{H} \end{matrix} \right\}$ , may also be obtained by boiling benzylamine with oxalic ether. It crystallises from boiling alcohol in white silky scales, dissolving sparingly in hot alcohol, but not in water and ether; it melts at  $216^\circ$ .

*Cyanbenzylamide*,  $\text{C}_7\text{H}_7.\text{NH}.\text{CN}$ , is obtained by passing dry cyanogene chloride into a cold ethereal solution of anhydrous benzylamine. The saturated solution is filtered from the benzylamine hydrochloride, the ether evaporated, and the residue placed in a vacuum. When recrystallised from ether it forms transparent plates, melting at  $33^\circ$ ; it is readily soluble in alcohol and ether, but insoluble in water. It does not combine with hydrochloric acid; on boiling it with this acid or with water it is converted into monobenzyl urea:—



*Tribenzylmelamine* or *tricyantribenzyltriamine*,  $(\text{C}_7\text{H}_7)_3(\text{NH})_3(\text{CN})_3$ . Cyanbenzylamide soon undergoes polymerisation, even when kept in

closed vessels or in a vacuum; the crystals melt, forming a heavy liquid which after some time become viscid, and at last solidifies; this transformation takes place more quickly on a water-bath. On treating the product with hydrochloric acid, tricyanotribenzyl-triamine hydrochloride,  $(C_7H_7)_3(NH)_3(CN)_3 \cdot 2HCl$ , is formed, which is sparingly soluble in water, and more freely in alcohol and ether, crystallising in needles. By decomposing this salt, the free base is obtained; it dissolves in water and alcohol and crystallises in laminæ. It melts at a much higher temperature than cyanbenzylamide, and forms a platinum double-salt.

*Dibenzylguanidine*,  $C \begin{Bmatrix} NH.C_7H_7 \\ NH \\ NH.C_7H_7 \end{Bmatrix}$ . The hydrochloride of this base is

produced by boiling an alcoholic solution of cyanbenzylamide and benzylamine hydrochloride; and the free base is formed by the action of dry cyanogen chloride upon pure dry benzylamine. The hydrochloride crystallises in laminæ, melting at  $176^\circ$ , and dissolving sparingly in water and more readily in alcohol; with platinic chloride it forms a crystalline double salt. By adding soda-solution to a solution of this salt, the base is precipitated as an oil which soon solidifies and crystallises from alcohol in colourless laminæ or plates, melting at  $100^\circ$ , and dissolving freely in water, alcohol, and ether.

*Dibenzyl sulpho-urea*,  $CS \begin{Bmatrix} NH.C_7H_7 \\ NH.C_7H_7 \end{Bmatrix}$ . An alcoholic solution of benzylamine is heated in a flask connected with a reversed condenser as long as hydrogen sulphide is given off. The product is evaporated and the residue crystallised repeatedly from alcohol. It forms large four-sided brilliant plates, melting at  $114^\circ$ , and dissolving in alcohol and ether, but not in water. On heating it with mercuric oxide it is converted into dibenzyl-urea.

*Benzylacetamide*,  $C_7H_7.C_2H_3O.HN$ , is formed when anhydrous acetic acid and benzylamine are heated together for some hours. It forms radiate needles, melting at  $30^\circ$ , boiling above  $250^\circ$ , and possessing a pleasant odour like that of flowers. It is very freely soluble in alcohol and ether, crystallising from these solutions only with great difficulty. Most remarkable is the great stability of this body, which is not acted upon by acids, and from which the acetyl cannot be removed by treatment with potash. By nitric acid it is converted into nitrobenzylacetamide, crystallising from ether in yellow deliquescent needles or laminæ. From this compound, too, the acetyl-group cannot be removed without complete destruction.

*Nitrobenzyl mercaptan*,  $C_6H_4(NO_2)CH_2.SH$ . In order to obtain an amidobenzylamine or benzyldiamine, nitrobenzyl chloride was acted upon by alcoholic ammonium sulphide, but the product formed was the mercaptan of nitrobenzyl. It forms small, colourless, shining, plates, melting at  $140^\circ$ ; is insoluble in water, but dissolves in alcohol and ether. The same compound is formed by boiling nitrobenzyl chloride with potassium hydrosulphide. By the continued action of ammonium sulphide or ammonia on this mercaptan, *nitrobenzyl disulphide*,  $C_6H_4(NO_2)CH_2S \begin{Bmatrix} \\ \\ \end{Bmatrix}$ , is produced, forming yellow microscopic crystals,



melting at  $89^{\circ}$ ; it is insoluble in water, but dissolves in alcohol and ether.

When nitrobenzyl chloride is heated with alcoholic ammonia in a sealed tube, a mixture of different bases is produced, amongst which there was found nitrotribenzylamine, the hydrochloride of which is insoluble in water, sparingly soluble in alcohol.

C. S.

### Kynurenic Acid and its Decomposition-product, Kynurine.

By O. SCHMIEDBERG and O. SCHULTZIEN.

KYNURENIC acid has been examined by Liebig, who assigned to it the formula,  $C_{16}NH_7O_5$  ( $C = 6$  and  $O = 8$ ), and by Schneider, who considered it to be  $C_{10}H_9NO_3$ ; the authors find that it is an acid of formula  $C_{20}H_{14}N_2O_6$ , the free acid containing  $2H_2O$  of crystallisation, and the barium salt being  $C_{20}H_{12}BaN_2O_6 + 3H_2O$ . It is obtained from dog's urine by evaporation and addition of hydrochloric or nitric acid; it is practically insoluble in water, either hot or cold, or impregnated with hydrochloric or nitric acid, but slightly soluble in alcohol or ether. With baryta-water in excess it yields a soluble basic salt, which furnishes a precipitate of mixed carbonate and neutral salt on passing carbon dioxide through the solution, an appearance which misled Liebig to the idea that the free acid was thrown down from the barium salt by carbonic acid.

When heated by  $265^{\circ}$  kynurenic acid evolves pure carbon dioxide and melts to a brown liquid. The product is mostly soluble in water, and furnishes crystals on evaporation of formula  $C_{18}H_{14}N_2O_2$ . This substance, *kynurine*, is anhydrous, melts at  $201^{\circ}$ , and gives a crystalline hydrochloride,  $C_{18}H_{14}N_2O_2 \cdot 2HCl + 4H_2O$ , and a crystalline platinum salt,  $C_{18}H_{14}N_2O_2 \cdot 2HCl \cdot PtCl_4$ ; it also gives a crystalline gold salt.

C. R. A. W.

### The Alkaloids of the Papaveraceæ. By H. LUDWIG (Arch. Pharm. [3], i, 33—38).

A SYNOPSIS of recent investigations relating to these alkaloids, giving their formulæ, physical characters, and principal reactions, also the dates of their discovery.

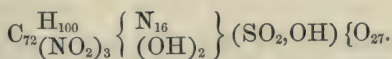
### A New Derivative of Albumin. By O. LOEW (J. pr. Chem. [2], v, 433—437).

REFERENCE is made to a former contribution (see this *Journal*, 1871, 409), of which this is a continuation, in which it was shown that by the action of a mixture of sulphuric and nitric acids, the radicals,  $NO_2$  and  $SO_2.OH$ , might be made to enter into an albumin derivative. By further research it was found that by acting on albumin in the cold with nitric acid, trinitroalbumin was formed,  $C_{72}H_{105}(NO_2)_3N_{18}SO_{22}$ . By treating this body successively with ammonia and hydrogen sulphide, then precipitating with an acid, another derivative, probably triamido-albumin, was obtained.



Calcium and lead salts of trinitro-albumin were prepared, in which 5 and 8 atoms of hydrogen were replaced by equivalent proportions of the respective metals.

By the prolonged digestion of albumin with nitric acid, Loew has prepared a body to which he assigns the name oxytrinitroalbumin and the following formula:—



T. S.

## Physiological Chemistry.

**Influence of Changes in Barometric Pressure on the Phenomena of Life.** By P. BERT (Compt. rend., lxxv, 491—494 and 543—547).

THE author discussed in a former paper (p. 831 of this volume) the action of various barometric pressures gradually produced, and now examines the effect of sudden alterations in pressure, such as those to which divers are exposed. Sudden increase of pressure seems to have little action. Sudden decrease, on the contrary, produces serious and even fatal effects. These are due to the gases which have been condensed in the blood during the continuance of the pressure, being set free on its removal, either in quantity, or forming bubbles more or less numerous within the blood-vessels. In the former case the circulation is at once arrested and death occurs almost instantaneously; in the latter, impairment of locomotor power, paraplegia or symptoms of cerebral mischief, such as squinting or madness are produced.

In the cases of paraplegia, the spinal cord undergoes softening with marvellous rapidity, but no trace of hæmorrhage has been noted. If the pressure to which the animal has been exposed does not exceed 5 atmospheres, it may be reduced to the normal in two or three minutes without any apparent bad result. If it has reached 6 atmospheres very serious symptoms may occur, and above 7 atmospheres these become constantly fatal. At 19 atmospheres paralysis and death can only be avoided by decreasing the pressure very gradually, five minutes for each atmosphere being too little, and transient paralysis having been noticed even when ten minutes per atmosphere was allowed. Divers who have not descended below 40 meters can generally be brought to the surface in safety, but rapid diminution of pressure would cause certain death if they descended to 70 or 80 metres. Such a descent is impossible as diving is at present practised, since the diver would be poisoned by oxygen; but the precautions mentioned by M. Bert in his former papers will render it possible in future; hence the importance of his present paper. The blood from an animal exposed to a pressure of 4 or 5 atmospheres frequently gives off bubbles of gas, and invariably does so when the pressure has reached 7 atmospheres. The quantity of oxygen in the blood increases with augmented pressure

but very slowly, while it diminishes very rapidly with decreased pressure. This seems to show that hæmoglobin is saturated with oxygen at ordinary pressures. The proportion of carbonic anhydride is not altered at all by increased pressure. That of nitrogen increases considerably, though it does not exactly follow Dalton's law.

T. L. B.

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**Comparative Researches on the Absorption of Gases by the Blood.—Estimation of Hæmoglobin.** By N. GRÉHANT (Compt. rend., lxxv, 495—498).

THE author's experiments show that normal arterial blood does not contain as much oxygen as it can take up. The amount obtained from blood from the carotid of a dog under ordinary circumstances was 16·3 volumes per cent.; after the inhalation of oxygen this rose to 23·3 per cent., but blood from the same animal saturated with oxygen by agitation with it contained 26·8 per cent. The quotient  $\frac{1}{2}\frac{6}{8}$  evidently depends on the rapidity of the circulation through the lungs, the healthy condition of these organs, the activity of the respiratory movements, &c. Thus the relation of the volume of oxygen actually contained in arterial blood to the maximum quantity which it can absorb exactly represents with tolerable exactness the effect produced by the respiratory efforts.

The amount of oxygen absorbed by specimens of blood from different animals of the same species varies with the amount of hæmoglobin they contain and the quantity of oxygen absorbed affords a ready method of quantitatively estimating the hæmoglobin. As part of the oxygen, however, is taken up by the salts of the blood and dissolved in the serum, the author prefers carbonic oxide, which is absorbed to a somewhat smaller extent than oxygen, and indicates the amount of hæmoglobin more exactly. Some experiments made by this method seem to show that hæmoglobin is destroyed in the liver.

T. L. B.

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**The Diffusion of Oxygen and the Process of Oxidation in the Organism.** By E. PLÜGER (Pflüger's Archiv. f. Physiologie, vi, 43—64).

THIS paper is devoted to the examination of the question whether the oxidation process takes place principally in the blood or in the tissues. The great rapidity with which oxygen disappears from the capillary blood of the systemic circulation, as contrasted with the great length of time required to exhaust the same blood of oxygen by the aid of heat and the Torricellian vacuum, has led Ludwig and his pupil, Worm Müller, to the view that the oxygen cannot disappear from the blood by diffusion alone, but that it must be used up by some reducing substance in the blood itself, as distinct from the tissues. From a comparison of the relative tension of oxygen in atmospheric air and the pulmonary blood, and the tension of oxygen in the arterial blood as distributed in the capillaries, Ludwig estimates the force which propels the oxygen from the alveoli of the lungs into the blood as five times greater than that which is available for the propulsion of the oxygen



from the blood of the capillaries into the tissues. In consequence of this a smaller quantity of oxygen must be diffused out of the blood than that which is diffused into it from the lungs. As, however, the same quantity of oxygen disappears from the capillary blood of the systemic circulation as is absorbed by the pulmonary capillaries in the same time, the oxygen which cannot escape by diffusion must remain in the blood, *i.e.*, the process of oxidation must take place there. This theory Pflüger regards as entirely erroneous and based on false calculations. The absorption of oxygen by the blood is dependent on the amount of hæmoglobin, and without this factor the partial tension of the oxygen in the alveoli could not suffice to diffuse into the blood more than one-eighteenth part of that required for the wants of the organism. He shows that with very great differences in the partial tension of oxygen in the air respired, the amount of oxygen absorbed remains constant, even under pressures at which the tension of oxygen is very much inferior to that of ordinary atmospheric air, and that, at the same time, without any appreciable alteration in the respiratory movements or interference with the vital processes. He finds Ludwig's calculations of the force of diffusion into the blood to be over-highly estimated and that into the tissues much under-estimated. He regards the wants of the cell, the only oxygen consumer in the organism, as sufficient to account for the rapid diffusion of the oxygen from the blood into the tissues by the physical laws of diffusion alone, without having recourse to the supposition that the disappearance of oxygen is due to any reducing agent in the blood itself.

D. F.

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**The Storing up of Fat in the Organism.** By F. HOFMANN  
(*Zeitschr. f. Biologie*, viii, 153—181).

HOFMANN seeks to determine by exact experiments in what way fat becomes deposited in the body, whether directly derived from the fatty elements of the food; or whether, as Toldt and Subbotin hold, it is derived from the splitting up of albuminoids; or whether, according to the views of Radziejewski, all fats must be first saponified and again undergo synthesis into neutral fat in the organism. To this latter conclusion Radziejewski was led by his experiments on the feeding of animals with fats which do not normally exist in the body. Hofmann criticises the experiments of Radziejewski, and thinks his conclusions are far wider than his premises, since these premises only prove that foreign fats are not stored up. The same is shown by Subbotin's experiments with spermaceti.

Hofmann's method consisted in starving dogs till all the body-fat was used up, and then feeding them with large quantities of fat, mixed with as small a proportion as possible of lean meat. After a few days the animals were killed, and the whole quantity of fat in the body determined. The fat found was considered first, as that derived from albuminoids. If the quantity found is not greater than might possibly be derived from albuminoids, it is considered that all the fat of the food has been burnt, and none deposited. If, on the other hand, a larger proportion of fat is found than can be accounted for in this way,



it can only have come from the food. This would not, however, decide the question whether the fat was stored up in the cells, for it might exist in the blood. If, however, not more than usual is found in the blood, and an amount corresponding to the quantity absorbed is found in the whole body, then it is considered as fat really deposited in the tissues of the body.

These points are all carefully attended to in the course of the experiments.

The first difficulty is in determining when the whole of the fat of the body has been used up by the process of starvation. Considerable differences in time are observed, according as the animal has or has not a large store of albuminoids, as well as fat, in its system. In general it is found that the fat of the body is almost entirely absorbed when the excretion of urea suddenly becomes greatly increased after a long period of starvation. This indicates that the wants of the organism require the combustion of a large amount of nitrogenous constituents to make up for the want of the fat which has now disappeared.

A dog so starved was found capable of assimilating considerable quantities of fat, when mixed with a small proportion of flesh. At the end of a few days, however, dyspeptic symptoms appeared, and almost pure fat was passed per anum. This was attributed to the fatty condition of the liver which was induced. The animal in five days increased in weight more than 21 per cent. of its weight on the last day of starvation. This increase was shown not to be due to water alone, nor to the small amount of lean meat of the food. Analysis of the blood likewise proved that this did not contain more than the usual proportion of fat.

The whole amount of fat in the body was determined in a novel way, consisting in the thorough mincing of the whole animal, and reduction of all its tissues to a uniform mass. Fractional analysis of this mass gave uniform results, and allowed of easy estimation of the whole fat in the body.

The tables show that in five days a dog had absorbed 1854.0 grams fat. If 130.7 grams be taken as the amount derived from albuminoids, a total of 1984.7 grams represents what was used by the organism.

Analysis found in the body 1352.7 grams, giving 632.0, which are considered to have undergone combustion. These figures show that a very large amount of fat may be absorbed from the food, and be deposited in the tissues. The deposit takes place principally in the liver and mesentery.

Hofmann questions whether it will be possible by the above method to determine whether fatty acids may undergo synthesis into fat, as it is impossible to give large quantities of soaps to animals without inducing serious derangement of the alimentary canal.

That fats are deposited in the organism, and not all burnt off, is also shown by the experiments of Pettenkofer and Voit, which are adduced. These prove that the amount of carbon given off by an animal receiving a large proportion of fat in its food is far below what would be required to cover the amount of fat consumed.

D. F.

**Formation of Sulphuric Acid and of Urea, and behaviour of Taurine in Animal Bodies.** By E. SALKOWSKI (Deut. Chem. Ges. Ber., v, 637).

SCHULTZEN considers the origin of urea and of sulphates in the urine to be due to the decomposition of bile acids first into cholalic acid (excreted in the fæces), glycocine, and taurine, and finally into urea and sulphates, the sulphur in the taurine being thus viewed as oxidized in the body.

When dogs and men were fed on food impregnated with taurine, no increase of sulphates in the urine was noticeable, but almost the whole taurine was excreted unchanged in the urine, no production of thio-sulphates being discernible, even when 15 grams of taurine were given in three days; when, however, vegetable feeders, such as rabbits, were experimented on, only about  $\frac{1}{4}$  or less of the taurine was unattacked, about  $\frac{1}{4}$  being excreted as an alkaline thiosulphate, and more than  $\frac{1}{2}$  as a sulphate, this latter being probably due to a secondary action, whereby the thiosulphate became oxidized.

It hence appears that in vegetable feeders the sulphates in the urine are at any rate partially derived from taurine, from the decomposition-products of the bile; the whole of the urea, however, cannot be due to these changes, inasmuch as the relative quantities of nitrogen and sulphur daily excreted are very different from those which should be present on Schultzen's supposition, the nitrogen being greatly in excess. Moreover, the author finds that the normal urine of dogs fed on bread and milk contains only  $\frac{2}{3}$  of its sulphur as sulphates, the rest being in the form of sulphurized organic substances, so that the *whole* of the sulphur of the taurine formed is not oxidized to sulphate.

C. R. A. W.

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**Action of Cupric Sulphate on Normal Urine.** By RAMON DE LUNA (Compt. rend., lxxv, 542).

By adding cupric sulphate to normal urine till a permanent bluish colour is produced, filtering, treating the filtrate with hydrogen sulphide, again filtering and evaporating, the author obtains three sorts of crystals. 1. Transparent, white, octohedrons, bulky, and very acid; soluble in water, giving with barium chloride a copious white precipitate, perfectly soluble in nitric acid, and with ammonium molybdate an abundant yellow precipitate. They are composed of sulphur, oxygen, hydrogen, nitrogen, and phosphorus. 2. Bulky, white transparent, prismatic crystals, very acid, soluble in water, giving with barium chloride a white precipitate, less soluble than the former in nitric acid. They contain hydrogen, oxygen, nitrogen, carbon, phosphorus, and sulphur. 3. An amorphous solid, fusible by heat, soluble in ether and in alcohol, insoluble in water, remains in the mother-liquor. Its ethereal solution yields on evaporation a crystalline mass of fine white prisms, resembling stearin in appearance. It is sublimed by heat, contains much carbon, is slightly acid and astringent, and somewhat deliquescent. It gives with barium chloride an abundant white precipitate, soluble in nitric acid, and very rich in phosphorus. It contains oxygen, carbon, nitrogen, hydrogen, and traces of iron, but no sulphur. The dark

residual liquid contains a blackish matter, which easily reduces cupric salts. The author is at present occupied in isolating it.

T. L. B.

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## Chemistry of Vegetable Physiology and Agriculture.

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### Chemical Examination of Sedum Acre. By ERNST MYLIUS (Arch. Pharm. [3], i, 97—110).

THE dried and powdered plant was subjected to the successive action of ether, of alcohol, and of cold, hot, and acidulated water.

Besides wax, chlorophyll, and other vegetable matters, rutin, and a small quantity of a peculiar alkaloid were obtained. The rutin, by boiling with dilute acids, furnished quercetin, and a sugar which reduced an alkaline copper solution. The uncombined alkaloid could not be obtained in the crystalline form, but it was strongly alkaline, and furnished soluble salts, of which the hydrochloride and nitrate could be crystallised by evaporation of their solutions *in vacuo*. It was not analysed.

W. A. T.

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### Kamala. By R. KEMPER (Arch. Pharm. [3], i, 118—119).

THE author points out the variable quality of kamala, as indicated by the proportions of ash yielded by different samples. In some cases the ash amounted to 50 per cent. and upwards.

W. A. T.

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### Amount of Nitrogen in Black Tea. By A. VOGEL (N. Repert. Pharm., xxi, 327—328).

SINCE tea may be considered, to a certain extent, as a means of nourishment, from the large amount of nitrogen it contains, the author thought it of interest to ascertain how much of this nitrogen is employed in the infusion. The tea examined gave 6.6 per cent. ash and 25.5 of extract, which was found to contain 2.8 per cent. of nitrogen, whilst the partially exhausted leaves contained 3.58. From this it would seem that by far the largest portion of the nitrogen is lost.

C. E. G.

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### Chinese Oil-Bean. By A. STÖCKHARDT (Chemischer Ackeremann, 1872, 122—125).

LITTLE is known of these beans; they are said to be used in China for the production of sweet-oil by pressure, while the pressed residue is manufactured into a kind of cheese. Two very small samples were examined: one yellowish-white, and of the size of small peas, the other still smaller, and black in colour. They belonged to the genus



*Phaseolus*. Their composition is given below, with the analysis of Chinese oil-bean cake by Dr. Voelcker.

	Yellowish oil-bean.	Black oil-bean.	Oil-bean cake.
Water .....	6.69	7.14	12.82
Albuminoids.....	38.54	38.04	45.93
Oil.....	20.53	16.88	5.32
Non-nitrogenous extrac- tive matter .....	24.61	27.79	24.52
Crude fibre .....	5.13	5.53	5.71
Ash .....	4.50	4.62	5.70
	100.00	100.00	100.00

Lupines differ from beans, peas, vetches, and lentils by containing no starch and much more fat and nitrogen. The Chinese oil-beans exhibit the peculiarity of lupines in a far higher degree.

R. W.

### Composition of Mulberry Leaves. By F. SESTINI (Versuchs-Stationen Organ, xv, 286—288).

THE leaves were obtained from Friaul in Italy. Four kinds were examined. The trees had all been manured with dung, and were usually stripped of leaves every second year. The following table shows the percentage of water in the fresh leaves, and of organic matter, ash, and nitrogen in the dry leaves, also the composition of the ash at various stages of growth:—

	<i>Morus alba silva- tica.</i>				<i>Morus alba domes- tica.</i>				Chinese Mul- berries.	Improved native.
	April 28	May 8.	May 12.	May 17.	April 29.	May 8.	May 12.	May 17.	August 24.	August 24.
Water .....	75.6	71.3	66.7	62.2	78.1	73.6	70.1	69.4	72.4	66.9
Organic matter.....	91.8	92.3	93.1	91.5	91.7	92.8	92.9	92.8	91.7	71.6
Ash .....	8.2	7.7	6.9	8.5	8.3	7.2	7.1	7.2	8.3	28.4
Nitrogen .....	6.1	5.3	4.6	3.8	6.1	4.6	4.6	5.6	4.1	5.1
Silica.....	9.4	10.6	10.7	11.6	9.6	10.4	10.8	15.2	8.0	15.9
Lime.....	21.1	24.6	26.0	28.3	24.3	26.3	27.6	28.9	31.7	33.3
Magnesia .....	7.6	9.7	9.0	8.8	7.5	8.2	8.0	7.9	11.2	10.7
Alkalis .....	15.6	17.1	16.9	19.0	16.6	17.9	18.2	19.2	24.1	16.9
Sulphuric acid .....	1.8	1.6	1.8	2.1	2.0	2.5	2.9	2.9	1.3	1.3
Phosphoric acid .....	24.8	21.7	20.0	16.9	20.1	19.6	18.1	13.5	18.1	12.1
Chlorine .....	2.1	1.7	1.2	1.1	1.6	1.3	1.3	1.1	.7	.8
Undetermined, and loss	17.6	13.0	14.4	12.2	18.3	13.8	13.1	11.3	4.9	.9

Liebig and Reichenbach found the Chinese and Japanese leaves richer in nitrogen than the French and Italian; their highest per-

centage was 3·36. Verson finds the nitrogen in the leaves at Görzer to be 4·69—5·84 per cent., thus differing from Liebig, and confirming the author's results.

R. W.

**Russian Summer-Rye.** By F. SCHWACKHÖFER (Versuchs-Stationen Organ, xv, 105—106).

THIS appears to be a little known variety of rye. Its produce is great, and remarkable for the high percentage of nitrogen present, and for other peculiarities. The weight of the corn per bushel was 68 lbs. The percentage composition was as follows:—

	Corn.	Straw.
Water.....	12·90	10·79
Albuminoids .....	17·34	4·60
Fatty matter .....	2·54	1·83
Non-nitrogenous extractive matter..	62·46	23·38
Crude fibre.....	2·66	53·92
Ash.....	2·10	5·48

The ash yielded to analysis the following percentage results:—

	K <sub>2</sub> O.	Na <sub>2</sub> O.	CaO.	MgO.	Fe <sub>2</sub> O <sub>3</sub> .	P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	SiO <sub>2</sub> .	Cl.
Corn ....	34·20	1·45	trace	12·40	trace	50·99	trace	1·01	trace
Straw....	30·84	·39	7·66	1·99	trace	4·90	5·64	48·50	trace

R. W.

**The Carthusian Pink as a Fodder.** (Chemischer Ackersmann, 1872, 62.)

THIS plant often grows in flower-gardens, is eaten readily by animals, and appears to be of high nutritive value. With a strong soil, and well manured, the produce is abundant. The analysis given below is that of the air-dried plant harvested before blossoming.

Water.....	12·44
Albuminoids .....	15·32
Fatty matter .....	3·45
Non-nitrogenous extractive matter	46·34
Crude fibre.....	12·08
Ash .....	10·37

100·00

R. W.

**Digestibility of Cellulose by Pigs.** By H. WEISKE-PROSKAU (Versuchs-Stationen Organ, xv, 90—97).

THE digestibility of cellulose has already been ascertained for cattle, sheep, goats, horses, rabbits, and men; but experiments were hitherto wanting in the case of pigs. Two pigs aged eight months, and of

similar weight, were fed for fourteen days on green oats and vetches just beginning to bloom; they received 15 lbs. per head per day. During the last seven days the food given and left unconsumed was analysed, the faeces were carefully collected, and the cellulose they contained determined. The dry food had the following percentage composition. The portion left uneaten contained more cellulose.

Albuminoids .....	16.56
Fatty matter .....	4.21
Fibre (free from ash and nitrogen).....	28.70
Non-nitrogenous extractive matter .....	40.27
Ash (free from carbon and carbonic acid) ..	10.26

Pig I consumed per day 872.96 grams of dry food, and yielded 312.75 grams of dry excrement, containing 40.11 per cent. of fibre. The pig had digested 41.06 per cent. of the fibre consumed. Pig II consumed per day 680.43 grams of dry food, and yielded 181.25 grams of dry excrement, containing 33.21 per cent. of fibre; it digested 56.68 per cent. of the fibre consumed. The mean percentage of fibre digested was 48.87 per cent. The proportion digested will doubtless vary a good deal with the character of the food. The pigs altered little in weight during the experiment.

R. W.

### Composition and Digestibility of the Fat of Meadow Hay.

By E. SCHULZE (Versuchs-Stationen Organ, xv, 81—90).

KÖNIG and Dietrich in their investigation of the digestibility of the fat of hay (*Chem. Soc. Jour.*, 1871, 1194), concluded that the true fats (the glycerides) were alone assimilated by sheep, and that the waxy matter present in the hay remained undigested; they separated the fat and wax by dissolving the ether extract in hot absolute alcohol, when on cooling the wax was deposited. The author shows that this conclusion is not warranted by their facts, which only prove that the fat of the excrement is richer in carbon than the fat contained in the food. In feeding experiments conducted by the author and Dr. M. Märcker, they found a very great difference in the digestibility of the fat of two samples of hay, which, nevertheless, exhibited little difference in their proportion of fat and wax. With one sample the diminution of fat in the excrement was so great that a portion of the waxy matter had apparently been assimilated; while with the other sample the diminution was so very small that a considerable part of the fat soluble in cold alcohol must have remained undigested. In the case of the second sample of hay, the ether extract of the excrement was separated by means of alcohol; it was found that there had been digested 40.1 per cent. of the fat soluble in cold alcohol, and 36.3 per cent. of the waxy matter. The author doubts whether the fat of hay soluble in cold alcohol is a glyceride. König determined its elementary composition, and found it to agree with that of a mixture of the glycerides of palmitic, stearic, and oleic acids; the author, however, failed to obtain glycerin from this fat, although from smaller quantities of true fat,



glycerin was readily obtained. He found a great portion of the fat to be saponifiable with litharge; the remainder was found to contain cholesterin. It appears unlikely that the fat of the excrement is contaminated by transformation-products; cholesterin and dyslysin are the only known bodies which are likely to enter into the ethereal extract (which König has shown to be free from nitrogen), and the latter is but little soluble in hot alcohol. Cholesterin having a high percentage of carbon, its presence in the excrement might possibly explain the high carbon found by König; but should it be present in distinct quantity, it will still have to be determined whether it is of animal or vegetable origin.

R. W.

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**Absorption of Humus-bodies by Plants.** By W. DETMER (Versuchs-Stationen Organ, xv, 284—286).

IN a previous paper (see this volume, page 521) Detmer showed that humic acid is a colloid body, and not taken up by plants. He repeats the experiment with the spores of an alga, *Euglena viridis*, and finds that neither humic acid nor neutral ammonium humate is absorbed by this plant from its solutions. Passing to crenic acid, he finds that this substance is capable of diffusion through membranes. In an experiment with recently germinated peas he found, by microscopical observation, that crenic acid had passed into the plant from its solution. The oxidation-products of humic acid appear, therefore, to be taken up by plants.

R. W.

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**The Balance between Evaporation and Precipitation.** By H. HOFFMANN-GIESSEN (Versuchs-Stationen Organ, xv, 98—104).

ACCORDING to Unger, a water-surface evaporates about three times as much as a plant of the same surface, and a forest in leaf evaporates much more than even a water-surface; T. Hartig, on the contrary, states that the evaporation from a forest is less than that from water or naked earth. According to Schübler, the daily evaporation during the season of active vegetation is for a water-surface 1 line, for growing turf 2—3 lines, for naked soil .60 line, and for a forest .25 line. The author determined the relation of rainfall to the evaporation from a water-surface during four months (May to September), continuing the experiment from 1855 to 58. A graduated cylinder was placed in a partially shaded spot in a garden; the fall or rise of the water level was noted each day, and then brought afresh to zero. During the whole 16 months of experiment, the rainfall was 45.68 inches, and the evaporation 55.86 inches. Since a part of the rainfall passes into the brooks and rivers, we can hardly believe that the evaporation from plants is as great as that from a water-surface. There is, however, to be considered the amount of water deposited as dew, and that absorbed by the soil from the atmosphere. Dew is comparatively insignificant. G. Wilhelm determined the dew at Kreuzlingen during 90 days, by

the difference in weight of covered and uncovered earth; it amounted to 1 centimeter. Dalton estimates the annual dew-fall in England at 5 inches. Lavyssée found the dew at Trinidad, from December 2 to May 1, to amount to 6 inches; he collected it on sponge. Little is known concerning the amount of water absorbed by soils from the atmosphere; according to W. Knop, indeed, it exceeds the rainfall; but more investigations are needed.

R. W.

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## Analytical Chemistry.

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**Detection of Chlorine, Bromine, and Iodine in Organic Substances.** By F. BEILSTEIN (*Deut. Chem. Ges. Ber.*, v, 620—621).

THIS method is founded on the well-known one of Berzelius for the detection of chlorine, bromine, or iodine in minerals, by means of cupric oxide and microcosmic salt. Some pure cupric oxide is placed on a loop of platinum-wire and heated for a short time to cause the oxide to adhere to the wire. If some of the suspected substance be now added and the loop again heated in the lower and inner edge of the flame of a gas-burner, the flame will assume a characteristic green or blue colour if either of the haloids be present. This reaction is applicable to all organic compounds, even such as chlorotoluene, methyl iodide, and chloroform.

C. E. G.

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**The Determination of Chlorine, Bromine, and Iodine by Carius's Method.** By B. TOLLENS (*Zeitschr. f. Chem.* [2], vii, 252).

THE author finds that bulbs of ordinary glass when heated with nitric acid of 1.2 sp. gr. to 160 or 220°, lose in weight to a considerable extent. Bulbs of Bohemian glass, on the contrary, scarcely at all. It is therefore necessary to avoid the use of tubes or bulbs of ordinary glass in the determination of chlorine, &c., by the method of Carius. Those of Bohemian glass may, however, be safely employed at moderate temperatures.

T. B.

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**Improvements in Chlorimetry.** By GEORGE E. DAVIS (*Chem. News*, xxvi, 25).

THE author takes advantage of the comparatively easy solubility of arsenious acid in glycerin, to prepare a solution of arsenious acid for chlorimetric purposes. He states that it possesses all the advantages, and none of the disadvantages of the solution prepared according to

Penot's original direction, or according to the modified plan preferred by some analysts. The standard solution is prepared thus: 13.95 grams of powdered arsenious acid are dissolved by the aid of heat in 40 c.c. of glycerin, and the solution diluted to one litre. Every 10 c.c. corresponds to 0.1 gram of chlorine. A drop of solution of indigo sulphate is used as an indicator, and the bleaching liquor is run into the arsenic solution, until the blue colour of the indigo is destroyed or changed to a brownish yellow.

In order to show that the method is trustworthy, the following results are appended:—

	Bunsen's method.	Arsenic dissolved in alkali and acid.	Arsenic dissolved in glycerin.
1....	36.72	36.64	36.64
2....	29.82	29.71	29.78
3....	25.86	25.80	25.80

J. W.

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**The Detection of Organic and other Nitrogenized Matter existing in the Atmosphere.** By ALFRED H. SMEE (Chem. News., xxvi, 25).

IN this communication the author describes a method which he has devised, and which he names "distillation by cold," by which he believes the detection and determination of ammonia and other organic impurities existing in the atmosphere will be greatly facilitated.

A glass funnel (usually of 8 or 9 inches) is drawn to a point and closed. It is supported in an ordinary stand, and filled with ice. Condensation of the watery vapour of the atmosphere then takes place; the dew collects into drops, which trickle down the outside of the funnel, and at last fall from the point, under which a small receiver is placed to catch them. The total quantity of liquid collected in a given time is measured, and the quantity of ammonia determined by Nessler's test. By this method of distillation by cold, the author found it possible to distil many substances which are decomposed at a high temperature. Thus many delicate odours of flowers were distilled by placing the flowers under a bell-glass sufficiently large to cover the funnel containing the ice. The odours were found to be more rapidly and completely abstracted by placing a dish with a little ether under the bell-glass at the time of distillation.

The paper is accompanied by tables, giving the results obtained in 107 experiments, together with the atmospheric conditions prevailing at the time. The experiments were made in a garden, bedroom, hospital wards, in the open country, &c. A few of the numbers obtained are here given by way of example:—



Fluid collected in minims.	Ammonia in grains per gallon.	Source.
150	1.9712	Erysipelas.
120	0.1791	Garden.
55	6.8807	*Drains.
90	2.1000	Bedroom.
—	2.9568	Stables.
150	0.0985	Victoria Park.

J. W.

**Estimation of Ammonia in Well and River Waters.** By  
H. FLECK (J. pr. Chem. [2], v, 263—273.

THE author considers that "Nessler's test" is the best reagent for estimating ammonia in waters, the delicacy of the reaction depending greatly on the alkalinity of the reagent. The process given by Chapman for preparing this test is the best.

That a compound of definite chemical composition— $\text{NHg}_2\text{I} + 2\text{HO}$  (*old atomic weights*  $0 = 8$ , &c.)—is produced in this reaction is fully established by the author's experiments. He takes advantage of this as follows:—0.5 to 1 cc. of solution of magnesium chloride (1:10) is added to 200 cc. of the water, unless this is already very hard, and then 4 cc. of Nessler's reagent. A precipitate quickly forms, especially on agitating the water; this, after settling, is collected on a small filter, washed with water, and dissolved, with the exception of the magnesia, in a solution of sodium thiosulphate (1:8), or poured over the filter, which is then well washed with water. All the ammonia present in the original water is now in this solution in the form of  $\text{NAg}_2\text{I}$ . By using a titrated sodium sulphide solution, the mercury is easily precipitated, and the quantity of ammonia present calculated.

This solution is made by fusing together 10 grams of potassium-sodium carbonate, and 4 grams of sulphur, dissolving the mass in water, adding 10 grams of caustic soda, and making up to 1 litre. It is titrated by means of a solution of mercuric chloride of known strength. 100 cc. of the sulphur solution used by the author corresponded to .5623 grm. Hg. On precipitating the mercury with this solution, the end of the process occurs, when a drop of the liquid on a piece of paper moistened with lead acetate, yields on drying a brownish ring, surrounding a black spot of mercury sulphide. This ring should not be very dark, otherwise too great an excess of the sulphur solution has been added. Any water, however turbid, may be thus tested, without previous filtering, as the sodium thiosulphate dissolves only the mercury compound.

M. M. P. M.

**Analysis of Potashes (Henry's Method).** By F. HAMEL (Chem. News., xxvi, 27).

THE following volumetric method has been devised for the estimation of the percentage of real potassium carbonate in commercial potashes.

The process depends, like many other technical plans for the quantitative separation of potassium and sodium, upon the comparative insolubility of potassium perchlorate in alcohol. 0.884 gram of dry sodium perchlorate corresponds to 1.0 gram of potassium carbonate, and a standard alcoholic solution of sodium perchlorate is prepared of such a strength, that every cc. corresponds to a known weight of pure potassium carbonate.

50 grams of the average specimen to be tested are treated with 100 cc. of cold water; the solution is filtered; an aliquot portion representing 5 grams of material subjected to the usual alkalimetric test; and the alkalimetric degree is noted. Another measure of the above solution, representing 1 gram of the potash to be tested, is saturated with acetic acid, the solution evaporated nearly to dryness, and the residue extracted with cold alcohol of 37°, and filtered. To the filtrate the titrated solution of sodium perchlorate is added, drop by drop, as long as a precipitate is observed; the number of c.c. consumed represents the proportion of pure potassium carbonate contained in 1 gram of the potashes under examination. It is unnecessary to reproduce here the simple details relating to the calculation from the above data, of the proportion of sodium carbonate present. No test analyses are given to show that the method may be relied upon as affording accurate results.

J. W.

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**The Separation by Heat of Arsenic from Arseniuretted Hydrogen in Marsh's Test.** By JOHN C. DRAPER (Scientific American, March, 1872, 195—211; Dingl. Polyt. J., cciv, 385—389).

To ascertain to what extent arsine,  $\text{AsH}_3$ , is decomposed by heat, the gas mixed with variable quantities of hydrogen, was passed at different rates through a tube heated in five places. When arsine, mixed with a considerable quantity of hydrogen, travels slowly, the greater part decomposes whilst passing over a single heated spot; but when the mixture is rich in arsenical gas and moves quickly, some of the arsine remains undecomposed, even after passing over five heated spots. The author subsequently found that arseniuretted hydrogen, moving at a rapid rate, could be completely decomposed by passing it over a bundle of heated platinum wires, placed in a narrow part of the reduction tube. The arsenic thus separated on the platinum can be easily subjected to reagents.

A. T.

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**The use of Magnesium in Marsh's Test for Arsenic.** By JOHN C. DRAPER (Scientific American, March, 1872, 179; Dingl. Polyt. J., cciv, 320).

IN consequence of the difficulty of obtaining zinc free from arsenic, it is proposed to replace that metal by magnesium in testing for arsenic

by Marsh's method. To do this it was found necessary to alter the form of the generator in order to have the action under control. The construction of the generator and the mode of operation are as follows:—A piece of wide glass tube is narrowed at one end by the blowpipe, and bent somewhat U-shape. Mercury is placed in this arm, and a funnel, with delivery-tube, &c., fitted to the wide end. The liquid is now poured into the apparatus, and, all being ready, magnesium ribbon is pushed round the bend, through the mercury, into the liquid.

A. T.

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**Examination of Bread and Flour for Alum.** By L. A. BUCHNER (Dingl. Polyt. J., cciv, 424).

LOGWOOD tincture, when added to bread containing alum, produces a dark-red coloration, and to bread free from this substance a straw-yellow (C. Moffat).

The author states that pure flour, when pressed between the fingers and moistened with a drop of the tincture, changes to brownish-yellow. Flour mixed with 1—2 per cent. of alum changes by this treatment to greyish-blue; with  $\frac{1}{2}$  per cent. a reddish-yellow coloration is produced, the edge of the spot being greyish-blue; with  $\frac{1}{4}$  per cent. the spot is yellow, the edge indistinct, but blue spots can be distinguished thereon by a magnifying glass.

A. T.

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**Some Reactions of Quinine and Morphine.** By F. A. FLÜCKIGER (Arch. Pharm. [3], i, 111—117).

EXPERIMENTS made with the view of ascertaining the comparative delicacy of the ordinary tests for quinine showed that the green coloration produced by chlorine and ammonia is capable of indicating the presence of 1 part of quinine in 4,000 to 5,000 parts of solution.

Bromine vapour, with subsequent addition of ammonia, also produces a green colour, which is perceptible when the solution contains only  $\frac{1}{20,000}$  of quinine.

Vogel's red reaction, obtained by the successive addition of chlorine, red or yellow prussiate of potash, and ammonia, is less delicate. About 1 part in 2,500 may be detected.

Similarly, by addition of chlorine water and ammonia, morphine may be detected in a solution containing  $\frac{1}{1000}$ . A red coloration is developed, which soon changes to brown.

The iodic acid reaction, however, is capable of indicating about one-tenth of this amount.

W. A. T.

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**Milk Analysis by the Ammonia Process.** By J. A. WANKLYN (Chem. News, xxvi, 28).

CASEIN, when distilled with alkaline permanganate yields 6.5 per cent. of "albuminoid ammonia." Since normal milk contains 4.0 per cent.



of casein, 100 parts of milk should give 0.26 part of albuminoid ammonia, and such is the result of the author's observations.

In order to examine milk by the ammonia process, the following method of procedure may be adopted. 5 c.c. of milk are diluted with pure distilled water to half a litre, and 5 c.c. of the dilute milk taken for analysis. 250 c.c. of water perfectly free from ammonia are placed in a retort, together with 50 c.c. of alkaline permanganate solution, and the 5 c.c. of diluted milk added. Distillation is then proceeded with as long as ammonia comes over, the ammonia in the distillate being estimated from time to time by the Nessler test in the usual manner.

The following are some examples of milk analysis by the ammonia process:—

*Milk yielding 12.92 per cent. of Solids, and 8 per cent. of Cream.*

	Quantity of milk taken.	NH <sub>3</sub> obtained.
I.....	100 milligrams.	0.27 milligram.
II.....	50       ,,	0.13       ,,

*Slightly Watered Milk. Solids, 10.20 per cent.*

	Quantity taken.	NH <sub>3</sub> obtained.
I.....	100 milligrams.	0.22 milligram.
II.....	50       ,,	0.095       ,,

*Highly Watered Milk. Solids, 6.18 per cent.*

	Quantity taken.	NH <sub>3</sub> obtained.
I.....	50 milligrams.	{ 0.075 milligram. 0.070       ,,
II.....	50       ,,	
Solids, 8-10 per cent.		

In order to translate these results into percentages of casein, all that is required is to multiply the *percentage* of ammonia by 100, and divide the result by 6.5. The figures so obtained represent the percentage of casein in the milk.

J. W.

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*Analysis of Waters in India.* By E. NICHOLSON (Chemical News, xxvi, 64, 80).

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*Estimation of Manganese.* By HUGO TAMM (*ibid.*, xxvi, 37); also by A. H. ALLEN (*ibid.*, 81).

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*Examination of Fixed Oils.* By H. LUDWIG (Arch. Pharm. [3], i, 1—33).

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*Estimation of Quinine.* By C. SCHACHT (*ibid.*, 38).

## Technical Chemistry.

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### On Pyro-plating. By J. B. THOMPSON (Chem. News, xxv, 26).

THE term pyro-plating is given to this process to distinguish it from the electro-plating, close-plating, and amalgamation processes, and, further, because the coating after deposition is driven into the surface of the metal by the aid of heat and atmospheric pressure.

It is employed whenever the above-mentioned processes are either unsuitable or impracticable, and is not confined to coating with silver, but can be applied to coating with gold, platinum, aluminium, copper, aluminium-bronze, and some other metals.

The rationale of the process is briefly as follows :—

The metal to be coated must be chemically clean. This end is attained in various ways according to the particular metal operated upon. Iron and steel articles are first boiled in caustic alkali, then mechanically cleansed under water with emery and wire brushes, and finally cleaned by generating nascent hydrogen upon their surface, the articles being suspended in a hot alkaline solution, and made the negative pole of a somewhat powerful battery. The time of immersion is judged by the experienced eye, the metal gradually assuming a more silvery appearance. When perfectly clean they are transferred to the plating bath, and the proper amount of metal is deposited upon them in the usual way.

The last stage of the process, which is in fact the only special peculiarity connected with it, consists in submitting the articles to the operation of firing. For this purpose a bright red heat is commonly employed, at least for articles which do not require tempering. For cutting instruments, the heat is more carefully watched, and not allowed to rise above 450° or 500° F. When the articles have attained the proper temperature they are withdrawn, and instantly quenched in cold water.

J. W.

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### Cement for Broken Glass and Porcelain Basins. (Dingl. Polytechn. J., cciv, 344).

HALF-AN-OUNCE of isinglass is well soaked in distilled water, the water is then poured off, and so much alcohol added as just to cover the isinglass, the solution being promoted by heat. A quarter of an ounce of mastic is now dissolved in  $\frac{3}{4}$  oz. of alcohol; the two solutions are poured together;  $\frac{1}{4}$  oz. of powdered gum-ammoniac is added; and the mixture is shaken well together, and evaporated on the water-bath, till the consistency of strong joiner's glue is attained. The cement thus prepared is poured into a glass, in which it soon solidifies to a jelly, and is then ready for use. It is warmed in hot water, or on the oven just

before using, and is applied by means of a brush to the perfectly clean, warm, fractured surface. The cement hardens in 24 hours.

W. S.

**Composition of English Quartz Bricks (Dinas Bricks)** (Dingl. Polyt. J., cciv, 419).

(a.) Average composition. (b.) Separated quartz lumps. (c.) The pumice-like binding material.

	a.	b.	c.
Silica .....	95.93	96.65	95.2
Iron oxide .....	0.48	2.20	2.0
Alumina .....	1.20		
Lime .....	2.15	0.5	2.3
Magnesia.....	0.24	0.14	0.17
Manganous oxide .....	trace	—	—

C. H. G.

**Manufacture of Aniline Colours.** By CH. LAUTH (Compt. rend., lxxv, 74).

MESSRS Girard and Laire having announced as new a method of obtaining the aniline colours without starting from rosaniline, the author states that a solution of this problem had been published by himself as early as 1861; he does not consider the danger of the use of arsenic acid in the preparation of aniline colours as great as has been represented by the same authors.

R. S.

**Observations relating to a Note of Messrs. Girard and de Laire, on the Colouring Matters derived from Diphenylamine.** By M. BARDY (Compt. rend., lxxv, 75).

THE author points out that the compound, prepared and called "methyldiphenylamine," by Messrs. Girard and Laire, is only an isomeride of the normal derivative of this name which he claims to have first discovered and utilised in the manufacture of the aniline colours.

R. S.

**The Dyeing of Leather with Coal-tar Colours.** By F. SPRINGMÜHL (Dingl. Polyt. J., cciv, 329—334).

THE leather is first put through a cleansing and dressing process, in which it is well washed with water to remove any alum that it may contain, then rubbed with yolk of egg, and worked on a wooden table till it lies quite smoothly thereon. In employing the aniline colours, free acids and alkalis must be carefully avoided. Very small quantities of free



acids cause the leather to become as fragile as paper, whilst alkalis, shrivel it up. As mordants, potassium chromate, very dilute alum solution, and best of all, ammoniacal salts, may be employed. The French lamb-skins form the best leather for taking these colours.

*Red.*—Soluble fuchsine is used for producing a red colour; its tint may be heightened by the addition of a small quantity of picric acid. The colouring matter is dissolved in more or less water at  $26^{\circ}$  to  $30^{\circ}$  C., and applied by means of a brush, when, if the leather be free from alum, a uniform tint is obtained, uninjured by subsequent washing or exposure to the air. Fuchsine soluble in alcohol may be used, but with less uniform or good results. Mordants cannot be used, with the exception of potassium chromate, which may be employed in small quantity. The purest and best colouring matter must always be chosen for leather dyeing.

*Violet.*—Aniline violet soluble in water, and mixed with a small quantity of aluminium sulphate, is applied just as the fuchsine is, and the article is well rinsed. The iodine-violet produces the most beautiful shades, which, however, resist the action of air and light for a short time only.

*Blue.*—The blue colours as a rule do not penetrate so well, nor will they produce uniform tints with the same ease as the foregoing. A very pure and intense blue is sought for, and this is diluted to the right point with water of  $30^{\circ}$  C. Deeper shades are obtained by repeated application of colour. As a mordant, generally a small quantity of potassium chromate is generally added. Alkali-blue has been made use of to produce magnificent tints upon fine leather. A very small quantity of acid is used to cause the colour to combine more easily with the leather; afterwards it is necessary to wash well, and dry at not too high a temperature.

*Green.*—Iodine-green is better suited for leather dyeing than any other green colour. This colouring matter may be used either in paste or powder, and is made into a very concentrated aqueous solution. The leather is first brushed over with solution of ammonium sulphate, and then rinsed in water, after which the colour solution at about  $35^{\circ}$  is applied rapidly. Picric acid is used to modify and lighten the green tint, and at the same time serves to render it faster: it must be applied after the leather has been dyed with the iodine-green.

*Yellow and Brown.*—Picric acid answers best for yellow. A very dilute solution is employed at  $20^{\circ}$  to avoid penetration of the leather. Coralline may be used with very fine leathers.

De Laire's brown is fixed by one of the afore-mentioned methods, and yields the best brown tint.

The tannin in the leather in many cases modifies the shade of colour very considerably, so as to render it a matter of difficulty to obtain clear and beautiful tints. The solubility of the colouring matter and the temperature employed are both most important items in leather colouring, and both advantages are available in the employment of the aniline colours and the derivatives of naphthalene. Various other coal-tar colours are described, which may be used with advantage.

W. S.

**Coralline Printed on Wool.** (Dingl. Polyt. J., cciv, 338).

THIS colouring matter, much used in dyeing wool, has been but little employed in printing on wool. The reason of this is, that in printing wool with coralline, the colour is almost sure to come in contact with acids in the various processes employed, when the red colour fades into yellow. In order to prevent this injurious effect, the author employs calcined magnesia with advantage, and with coralline soluble either in water or in alcohol. The resulting colour is a rich Turkey-red, which maintains its intensity and brilliancy for years. This red is about 30 per cent. cheaper than cochineal red, and has the advantage over the latter in that, by washing in water containing calcium carbonate, it does not pass into a blue shade, the only disadvantage being that of its fading in contact with strongly acid colours, if the acid be more than sufficient to neutralize the magnesia. The following mixture is recommended for printing :—

80 grams coralline.  
 $\frac{1}{16}$  litre glycerin.  
 $\frac{1}{4}$  „ water.  
 140 grams magnesia, well stirred up  
 with  $\frac{1}{4}$  litre of water.

The whole is thickened with  $\frac{3}{4}$  litre of gum-water (500 grams to the litre), and printed, steamed, and washed in the usual way.

Coralline may also be printed on cotton, the colour being thickened with starch and egg-albumin in addition to magnesia. This mixture must be used fresh, as in time an insoluble compound is formed between the magnesia and the albumin.

W. S.

**An important Advance in the Manufacture of Paper (Cellulose Paper).** (Dingl. Polyt. J., cciv, 341—342.)

THE use of wood for paper-making is the important advance referred to in this paper. Völter, of Heilbronn has also invented a wood-cutting machine, with which the wood may be separated into the finest fibres or filaments. As this separation of wood into fibres requires much machinery and mechanical power, many chemists have endeavoured to devise a chemical means of effecting this object, but only Sinclair and Tessié du Mothay have met with practical success. Sinclair's process till lately appeared to furnish the best and cheapest product; just recently, however, Unger has improved considerably upon it. Sinclair treats the wood with strong soda-lye under high pressure, viz., about 14 atmospheres. The fibre is bleached with chloride of lime, as usual. Unger, in his process, requires only a pressure of five to six atmospheres, half the quantity of soda, and only a fifth part the quantity of chloride that Sinclair does. In this process the wood-stuff does not require grinding, which is a considerable advantage, and furnishes, without mixing with rag-stuffs, a good substantial paper.

W. S.

## PAPER READ BEFORE THE CHEMICAL SOCIETY.

XXXII.—*Mineralogical Notices (continued).*

By Professor STORY-MASKELYNE and Dr. FLIGHT, of the Mineral Department, British Museum.

## 8. ISOPYRE.

UNDER the name of isopyre various massive minerals are to be met with in European collections. The original specimens to which the name was given, in 1827, by Haidinger, are now in the British Museum. They were brought by Mr. Allan, in 1824, from St. Just, and were analysed by Turner (*Phil. Mag.*, iii, 263). The colour is of a jet black, carrying a few red spots resembling those of blood-stone; the streak is of a pale greenish grey, and the mineral acts slightly on the magnetic needle. Its hardness is 6·5, specific gravity, 2·912, and it exhibits a conchoidal fracture. One specimen occurs on granite associated with tinstone and tourmaline (schorl).

An analysis of this black specimen gave the following numbers :—

Silicic acid (uncombined) .....	14·335
Silicic acid (combined) .....	31·818
Alumina .....	12·594
Iron oxide .....	3·026
Iron protoxide .....	15·909
Lime .....	13·208
Magnesia .....	1·665
Potash .....	1·154
Soda .....	0·698
Lithia .....	Trace
Copper oxide .....	1·096
[Fluorine* .....	2·278]
Water .....	0·851
	<hr/>
	98·632

By testing the mineral with potash, it became evident that a portion of the silicic acid, amounting to 15·186 per cent., was present in the form of opal, and that it was mixed with a mineral, the formula of which would nearly accord in type with that of a felspar. It also con-

\* From the percentage of fluorine, as determined, 3·934, less probably than that actually present, a deduction has been made to compensate for the oxygen included in the bases.



tains from 8 to 9 per cent. of fluoride. A discrepancy is evident in Turner's analysis, from his having missed the fluorine, and not having determined the proportion of the two oxides of iron.

From the same neighbourhood of St. Just a dark-brown mineral, compact, massive, and with a conchoidal fracture has also received the name of isopyre. Its semi-vitreous lustre is in contrast with the vitreous lustre of the mineral of Haidinger. It carries opal in botryoidal forms in cavities, and a dendritic accompaniment, probably of pyrolusite, or perhaps melaconite, occurs occasionally as an infiltration. Native copper occurs with it very sparsely. Its hardness is 7, and it has the following percentage composition:—

Silicic acid .....	93·042
Iron oxide .....	3·229
Copper.....	1·381
Water .....	2·718
	<hr/>
	100·370

The iron in the above specimen has been calculated as oxide. To judge by a qualitative test, however, it is probable that some portion of the metal is present as protoxide. The powdered mineral had a buff colour, which changed on ignition to a light brick red.

A dark olive-green compact mass, with a conchoidal and rather splintery fracture, slightly translucent, and with a waxy lustre, occurs at Suckasunny, in New Jersey. It has also been called isopyre. A similar mineral from the same locality closely resembles the brown Cornish variety in colour and characters. The green variety above mentioned, when finely powdered, is of a pale greenish grey colour, changing by ignition to buff. It has the following composition:—

Silicic acid .....	92·790
Iron oxide .....	2·101
Lime .....	0·354
Magnesia.....	• 0·354
Water .....	4·068
	<hr/>
	99·667

Apparently no portion of the small amount of iron present in this specimen is in the form of the lower oxide.

A liver-brown mineral (I) associated with one (II) having the appearance of jasper, and also coming from St. Just, closely resembles the mineral second on this list. The jasper-like mineral associated with it presents in parts the dull aspect and other characters of massive eisenkiesel; elsewhere its characters are those of a jasper opal. Iron

ochre, pyrolusite, and melaconite accompany it in the former specimens. It occurs in a siliceous matrix with some of the characters of a gossan, and is associated with quartz and a finely grained chlorite and ferric oxide.

These two minerals have the following composition:—

	I.	II.
Silicic acid.....	73·153	76·215
Alumina.....	0·055	0·151
Iron oxide .....	9·531	9·049
Iron protoxide .....	10·621	8·857
Lime .....	0·297	0·319
Magnesia .....	0·111	0·201
Water.....	5·462	4·758
Copper oxide.....	—	0·629
	<hr/> 99·230	<hr/> 100·189

After treatment with potash, I. left a residue amounting to 25 per cent., and II. one of 25·630 per cent. And it is evident that these minerals consist of opal in different degrees of impurity.

The presence in all these varieties of opal of ferrous oxide may explain the mineralogical similarity to which their association under the name of isopyre in our collections is due. Their source has probably been mineral waters charged at once with silica and a ferrous carbonate. That they are only the more characteristic specimens, occurring in large deposits of the same kind, is evidenced by the character of the lodes charged with copper ores at Botallack or the Bilston mines, where the neighbouring granites offer the conditions for furnishing the material.

#### 9. PERCYLITE.

Among the minerals in the British Museum collection, especially interesting from its rarity, or rather from the specimen there exhibited having been till now unique, is one named Percylite by Brooke (*Phil. Mag.*, xxxvi, 131) after Dr. Percy, who analysed it, and assigned to it the formula  $Pb_2Cl_2O.Cu_2Cl_2O.H_2O$ . This well known specimen presents beautiful blue crystals, belonging to the cubic system, which are associated with red iron oxide, quartz, and gypsum, and are remarkable also for a notable amount of gold being disseminated through the specimen; the locality assigned to it is Sonora, Mexico. The mineral to which this notice is devoted is Percylite from another locality, namely, South Africa.

The specimens in question are found sometimes in very minute but confused crystals, generally, however, massive, as a coating or as a

vein in association with anglesite, cerussite, and chlorargyrite. It was almost impossible, from the specimens at our disposal, to obtain any crystals sufficiently good for measurement. One fragmentary crystal, however, gave three planes in a zone [100, 110], which corresponded with those of the rhombic dodecahedron. That the crystals, however, really belong to the cubic system may be accepted as proved by their inertness when placed in a beam of polarised light.

Among the physical characters recorded by Dr. Percy is the change this mineral undergoes by the action of heat, the blue colour changing to emerald-green, and reappearing on cooling; the South African specimen also exhibited this property. The analysis of very carefully picked specimens gave numbers which show that the percylyte was still mixed with some of its associated minerals, more especially anglesite and chlorargyrite, from which it is necessary to disentangle it. Its composition was—

Lead sulphate .....	22·979
Silver.....	8·979
Lead .....	37·640
Copper .....	8·782
Chlorine.....	13·368
Carbonic acid .....	1·394
Water .....	2·871
Oxygen.....	not determined.
	<hr/>
	96·013

By deducting the associated anglesite, chlorargyrite, and cerussite, the residues give numbers whose equivalent ratios are—

Lead .....	0·295
Copper .....	0·277
Chlorine .....	0·293
Water .....	0·319

These ratios correspond with those of percylyte.

Another mineral from South Africa may be introduced here, as a sequel to the last, rather from its colour and locality than from the mineralogical interest attaching to it under the incomplete conditions offered by a single specimen for the investigation of its nature. In point of fact, a single specimen, coated with but a thin layer of the mineral in question was all that we had to operate upon.

On a gneissoid gangue, rich in muscovite and quartz tinted with copper, is found a layer of a blue (inclining to lavender blue) mineral in botryoidal forms, and carrying in places a green incrustation, through which this blue mineral appears also to be interspersed. In places, also, the blue mineral appears in fibres, apparently crystals,



generally drused with smaller blue crystals. The substance analysed was picked from a considerable portion of the specimen, and gave the following numbers:—

Silicic acid (soluble) . . . . .	18·894
Arsenic acid . . . . .	9·791
Phosphoric acid . . . . .	11·749
Sulphuric acid . . . . .	3·448
Carbonic acid . . . . .	0·997
Copper oxide . . . . .	32·154
Iron oxide . . . . .	4·359
Alumina . . . . .	2·274
Gangue . . . . .	10·922
Water (by difference) . . . . .	5·412
	<hr/>
	100·000

It is probably chrysocolla mixed with two minerals: one of the brochantite group, probably langite, and the other a copper arsenophosphate.

#### 10. VANADINITE.

Among a number of ore-specimens brought from South Africa by Mr. Wollaston, there were included the perylite already described, and a mineral of a chestnut-brown colour, high resinous lustre and considerable specific gravity. The specimens were lying loose among other ores, so that the crystals, of which the specimens almost entirely consisted, were much bruised. They presented great similarity to mimetosite, but their true character was not difficult of recognition. They consist in fact of vanadinite in a state of remarkable purity. The specific gravity of a large specimen is 6·661, and the analysis gave the following numbers:—

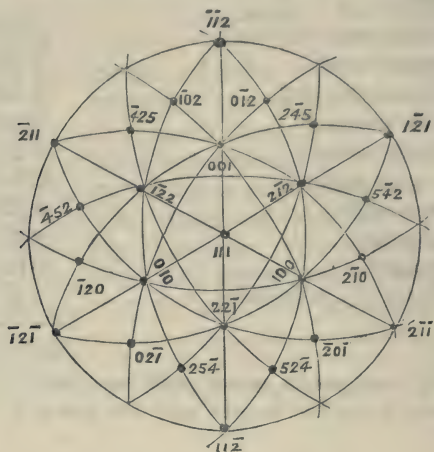
Lead oxide . . . . .	78·416	77·770
Vanadic acid . . . . .	19·239	18·570
Chlorine . . . . .	2·56	—

The second determination of vanadic acid was made by Professor Roscoe's method of titration with permanganate. It is difficult to reduce the acid to its lowest degree of oxidation unless the solution be of a certain degree of concentration.

Molybdenum, chromium and phosphorus, which were sought for, are one and all absent.

The crystals of the South African vanadinite carry faces of the following forms: the protoprism  $\{2\bar{1}1\}$  and the dirhombohedral  $\{100, \bar{1}22\}$ ; occasionally the pinakoid  $\{111\}$  and the discalohedron  $\{201\}$ , which seems to be accompanied by the correlative form  $\{425\}$ .

The faces of the last forms are very minute and only to be detected on a few angles of the crystals; their positions on these, however,



seem to preclude the view of their being a hemisymmetrical development of the dipyrmaid.

The crystals exhibit a slight shear, rendering the accurate adjustment of the zones impracticable. The following are the measurements obtained:—

			Calculated.
100	111	= 39° 21'	39° 23'
110	$\bar{1}22$	= 78° 42'	78° 46'
100	$22\bar{1}$	= 36° 59'	36° 59'
100	010	= 67° 8'*	66° 39'
$22\bar{1}$	$20\bar{1}$	= —	39° 43'
100	$20\bar{1}$	= 29° 26'	28° 48'
$11\bar{2}$	$20\bar{1}$	= 45° 58'	45° 45'

The faces of the disclenohedral pyramid and of the prism, are too dull, and the latter too much sheared for accurate measurement.

## 11. URANITE.

In a rather dense gossan containing limonite and quartz from the neighbourhood of Redruth, there occurs a mixture of minerals that may hereafter prove to be of considerable interest. A bright lemon-yellow, ochrey and somewhat dense incrustation is entangled with microscopic green crystals, but is obviously too mixed a substance to

\* This would give 100 111 = 39° 40'.

offer much hope of determining its true character. The green mineral presents, however, the characteristic features of uranophyllite or copper uranite, and probably all the copper found by analysis in the mixed substance should be appropriated to that mineral. The following is the percentage composition of the mass separated as much as possible from the gossan accompanying it:—

Copper oxide .....	4·058
Bismuth oxide .....	2·556
Lead oxide .....	2·101
Uranium oxide.....	62·496
Lime .....	2·412
Phosphoric acid*.....	14·040
Arsenic acid.....	1·181
Sulphuric acid.....	0·952
Water (at 100°) .....	0·215
Water (over 100°) ....	10·377
	<hr/>
	100·388

Abstracting from these results 47·85 per cent. of uranophyllite the residue might afford an object for ingenious speculation. Not, however, allowing ourselves to be led astray into this path, we would simply indicate that the recent discovery in the Weisser Hirsch mine at Schneeberg of walpurgine and trögerite gives to the simultaneous presence of bismuth and uranium in association with arsenic an interest that seems to justify our placing on record this interesting combination of elements as occurring in a Cornish specimen. A considerable similarity in the general aspect of the minerals might even justify the hope that these new minerals may yet be found in the neighbourhood of the mixed masses of which the analysis is here given.

## 12. ANALYSES OF SOME PISOLITIC IRON ORES FROM NORTH WALES.

A specimen from near Llanwrchymedd, Anglesea, had the following composition:—

\* I wish to direct attention to two important errors in one of the tables in the *Anleitung zur quantitativen Chemischen Analyse*, of Fresenius, fifth edition, published in 1866. They are to be found in that fourth table of the Appendix to which many chemists turn at the conclusion of an analysis to calculate the amount of some constituent of each precipitate that has been weighed. On page 987, and in the column with the heading 4, when the amount of pyrophosphate of magnesia having been determined, that of the phosphoric acid is required, the number 1·55856 should be 2·55856. On page 989, in the column with the heading 9, where the amount of oxygen in a certain weight of lime is given, the number 1·57143 should read 2·57143. The latter misprint also occurred in two of the English editions of this work, edited by J. L. Bullock, and published, the second edition in 1854, and the third edition in 1860.—W. F.



Silica .....	13·917
Silica (combined) .....	1·799
Phosphoric acid .....	11·36'
Carbonic acid .....	16·038
Iron oxide.....	10·566
Chromium oxide .....	trace
Iron protoxide .....	28·946
Lime .....	12·309
Magnesia .....	1·914
Water and organic matter .....	4·084

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100·937

Two specimens from Pwlllely, a nodule and the massive rock enclosing it, were also examined. The nodule had the following composition:—

Insoluble part:

Silica (combined) . ....	5·150
Silica .....	6·565
Iron oxide and lime ....	0·754
Organic matter .....	0·736

Soluble part:

Iron oxide .....	11·686
Alumina .....	1·640
Iron protoxide .....	5·408
Lime .....	37·479
Magnesia.....	trace
Phosphoric acid .....	24·415
Carbonic acid.....	0·721
Water .....	2·484

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97·038

Fluorine, amount not determined.

The matrix, on the other hand, had the following composition:—

Iron oxide .....	11·606
Alumina .....	9·391
Iron protoxide .....	29·861
Lime .....	1·499
Phosphoric acid.....	1·012
Carbonic acid.....	9·699
Water .....	5·993
Insoluble portion .....	28·439
Organic matter .....	1·926

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99·426

## 13. PRASINE.

A specimen of the white so-called olivenite on quartz was some time back sent by Mr. Talling to the British Museum. A remarkable bluish-green, botryoidal, lustrous, slightly fibrous, but otherwise uncrytallised mineral is associated with it. Subsequently, Mr. Talling sent other specimens of this last mineral, some of them presenting an almost emerald-green colour, but without olivenite. On one of these specimens the green mineral in question has evidently been formed round crystals of cuprite, which having entirely disappeared, have left this green mineral as a slightly translucent shell. In other cases it occurs as an epimorphous deposit on chalcedony, which has filled the spaces between crystals of other minerals that have disappeared, or which coats crystals of quartz. It is invariably met with, so far, as an associate of quartz, small quantities of kaolinite and chrysocolla, pseudomorphous after malachite, and a cuprous allophane in some instances accompanying it. The composition of this mineral is that of prasine or ehrlite; more correctly it represents that member of the pseudomalachite group of minerals, which contains two equivalents of cupric hydrate and one equivalent of water. The normal pseudomalachite contains three equivalents of cupric hydrate (Rammelsberg), ehrlite or prasine, containing, as above, two equivalents of cupric hydrate and one equivalent of water, while tagilite contains one equivalent of cupric hydrate and two equivalents of water (Hermann and Field).

Analysis gave the following results:—

		Oxygen.
Copper oxide .....	64.763	13.05
Phosphoric acid .....	23.446	13.21
Arsenic acid.....	1.494	0.52
Water .....	8.634	7.67
Quartz .....	0.956	—
Alumina .....	1.030	0.48
Water (hygroscopic) .....	0.407	—

100.730

Of the combined water, 0.163 per cent. passed off at 100° C., 1.005 per cent. at 190°, and 7.466 per cent. at a visible red heat.

The hardness of the mineral is 4.5, being less than that of apatite, and the specific gravity 3.98, which is probably slightly too low, in consequence of the cellular structure of the substance. The streak is of a pale, decidedly bluish-green tint, much paler than the massive mineral. The botryoidal structure of the mineral is peculiar, forming reticulated clusters. The fracture has the waxy character usually distinguishing a phosphate, as compared with the more metallic lustre of a corresponding arsenate.

# ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

## Physical Chemistry.

**Researches on Fluorescence.** By EDUARD HAGENBACH (*Pogg. Ann.*, cxlvi, 65—89, 232—256, 375—405, and 508—538).

THESE papers contain a detailed description of the fluorescence phenomena exhibited by the following substances:—1. Solution of Morinalumina. 2. Naphthalene red. 3. Oxidised Brasilin. 4. Nitrate of Chrysaniline. 5. Thiomeic acid (*Erdmann, Journ. f. prakt. Chemie*, xxi, 291). 6. Extract of Soot. 7. Amide of Phthalic acid. 8. Extract of *Datura Stramonium*. 9. Extract of the seeds of *Peganum Harmala*. 10. Amide of Terephthalic acid. 11. Sulphate of Quinine. 12. Aesculin. 13. Fraxin. 14. Infusion of *Lignum nephriticum*. 15. Infusion of Quassia wood. 16. Extract of Sanders. 17. Litmus. 18. Infusion of Turmeric. 19. Barley sugar. 20. Sandarac. 21. Guajac. 22. Purpurin. 23. Archil. 24. Safflower. 25. Dichloranthracene. 26. Photene. 27. Petroleum. 28. Bisulphanthraquinone. 29. Fluorspar. 30. Uranium glass. 31. Uronic Nitrate. 32. Ordinary Glass. 33. Phthaleine of resorcin (?). 34. Fluoranine. 35. Barium Platino-cyanide. 36. Chlorophyll.

The apparatus and the methods employed by the author were the same as those described in a former communication (*Pogg. Ann.*, cxli, 245). An alabaster, glass, or white earthenware plate was placed on a level with the fluorescent liquid, and by throwing the image of an illuminated slit, half upon the liquid, half upon the plate, the different refrangibilities of the unaltered light reflected from the plate and of the altered light reflected from the liquid could easily be examined by a prism whose edge was parallel with the slit. The light allowed to pass through the slit was either white sunlight, or light from a particular portion of the spectrum, or light which had gone through one or several coloured glasses. Every substance was also exposed to the light of the induction spark in hydrogen and nitrogen.

The measurements refer to a scale given in the paper above cited, in which the Fraunhofer lines occupy the following positions:—

A	a	B	C	D	E	b	F	G	H <sub>1</sub>	H <sub>2</sub>
0	34	63	90	188	309	331	420	657	831	888

Attention was chiefly paid—1, to an exact determination of the limits and of the maxima and minima of the fluorescence spectra; 2, to the examination of the absorption spectra; 3, to the effect which a change of the exciting light produces in the fluorescence spectrum.

The statement recently made by Lommel, that the fluorescence spectrum of naphthalene-red extends beyond that of the exciting light, was, on being submitted to a most careful examination, *not* confirmed, whilst the law of Stokes, according to which the fluorescent rays are always less refrangible than the exciting rays, was found to hold good in every case, as well as the other law of the same philosopher, that the same rays which are capable of producing fluorescence within a sub-



stance are also absorbed by it. As an instance of the effects of a change in the exciting light, the results obtained with thiomelic acid may be cited:—

Light passing through a red glass produces a feeble red fluorescence, extending from 30 to 44 (max. at 43).

Light passing through a dark-yellow glass produces an orange fluorescence, extending from 30 to 81.

Light passing through a light-yellow glass produces a yellow fluorescence, extending from 30 to 104 (max. at 54).

Light passing through a green glass produces a greenish-yellow fluorescence, extending from 32 to 78 (max. at 57).

Light passing through a blue glass produces a green fluorescence, extending from 37 to 117 (max. at 76).

Light passing through a violet glass produces a bluish-white fluorescence, extending from 37 to 111 (max. at 78).

The feeble extent to which the blue and violet rays excite red fluorescence is probably the cause that the spectra do not always commence at 30.

The fluorescence spectra obtained by the alcoholic solution of the amide of phthalic acid and the alcoholic extracts of *Datura Stramonium* and of *Peganum Harmala*, show such resemblance as to justify the conclusion that they are caused by one and the same substance.

In some cases the position of the absorption bands is influenced by the nature of the solvent; in the alcoholic solution of chlorophyll, for instance, they lie perceptibly nearer the red end of the spectrum than in the ethereal solution. This displacement is greatest in the more refrangible portion; thus, of the two bands marked as VII and I, the first is displaced only 18, and the latter 3·6 divisions of the author's scale. Now as a shift of 18 divisions in the portion of the spectrum near G, and a shift of 3·6 in the region containing the band I, both correspond to an increase of wave-length by 3·5 millionth parts of a millimeter, it follows that the difference in wave-length of the light extinguished by an alcoholic and by an ethereal solution is the same for the different parts of the spectrum.

The maximum of fluorescence and absorption, or the greatest change of refrangibility in the ordinary spectrum, does not exactly coincide with, but is very near the maximum of intensity in the fluorescence spectrum.]

The absorption-bands in the spectrum of light which has traversed green leaves, which are caused by chlorophyll in the solid state, correspond with those produced by chlorophyll in solution, but they are shifted towards the red end of the spectrum with greater displacement at the violet end.

*Duration of Fluorescence.*—Becquerel had already shown that certain solid fluorescent substances are also phosphorescent, but no fluorescent liquid had as yet with certainty been proved to be phosphorescent. In order to avoid the disturbing influence of the fluorescent glass vessel, the author constructed an apparatus in which the exciting light was thrown directly upon the free surface of the liquid; but none of the liquids examined by him showed any signs of phosphorescence.

*Fluorescence in the Spectrum, or Fluorescent Spectra.*—The author's experiments lead him to believe that light of every degree of refrangi-

bility is capable of exciting fluorescence, which in the more refrangible part is observed to extend beyond the line H, whilst our eyes would, for obvious reasons, not perceive any fluorescent light which may be produced beyond the other end of the ordinary spectrum.

The number of maxima of fluorescence is very different for different substances, as we observe—

7	maxima in a fresh solution of chlorophyll,	
6	„ in altered solution of chlorophyll,	
5	„ in an extract of lampblack,	
4	„ in barium platinocyanide,	
3	„ in naphthalene red,	} and in other sub- stances.
2	„ in oxidised brasilin,	
1	„ in the solution of morin-alumina,	

The maxima and minima of intensity can be easily distinguished in the case of some substances, and less easily, or scarcely at all, in the case of others.

*Relation between Fluorescence and Absorption.*—Stokes's observation that the absorption-bands of fluorescent bodies correspond generally with maxima of fluorescence, has been confirmed in nearly all the substances examined by the author. A few in which absorption was not accompanied by fluorescence may be assumed to be mixtures of a fluorescent and a non-fluorescent substance. Solid or dissolved uranic nitrate, however, which has no fluorescence maxima corresponding with its absorption-bands, seems to form a real exception to the above rule, as it can scarcely be looked upon as a mixture.

*Spectrum of the Fluorescent Light, or Fluorescence Spectrum.*—The maxima of fluorescence in the spectrum do not always correspond with maxima in the spectrum of the fluorescent light; the solution of chlorophyll, for instance, shows seven maxima of fluorescence in the spectrum, but only two maxima in the spectrum of the fluorescent light. From Pierre's hypothesis, that the substances producing an intermittent fluorescence spectrum are mixtures, it would follow that those compounds which cause the fluorescence of chlorophyll must in all plants be mixed in exactly the same proportion. As this can scarcely be admitted, the author thinks that Pierre's hypothesis may apply to some, but certainly not to all cases of intermittent fluorescence spectra. The author can also not confirm the following results of Pierre:—(1.) That the fluorescence colours are homogeneous. (2.) That the same fluorescence colours prevail throughout the whole length of the derived spectrum, or that the composition of the fluorescence spectrum is independent of the nature of the exciting light. (3.) That those colours in the derived spectrum are most intense which are in the immediate neighbourhood of the commencement of fluorescence.

The first of these propositions is disproved by the fact that in the case of thiomelic acid the fluorescence begins already at C, whilst the fluorescence spectrum contains rays between F and G. The second proposition does not agree with the fact that the fluorescence spectrum is shortened when it is excited by rays of a lower refrangibility; and that the position of the maxima of fluorescence is different for



exciting rays of different refrangibility. The third proposition does not agree with the author's observation that in the case of naphthalene fluorescence begins at 139 (on the author's scale), whilst the maximum of light in the fluorescence spectrum lies at 171.

*Influence of the Solvent.*—The position of the maxima and minima of fluorescence varies more or less with the nature of the solvent employed.

*Influence of the State of Aggregation.*—Some substances exhibit fluorescence only in the one state of aggregation; others are fluorescent both in the solid and in the liquid state.

*Relation between Fluorescence and Phosphorescence.*—In order to decide the question whether a fundamental difference, or only a difference in degree, exists between these two phenomena, it will be necessary to show that some fluorescent liquids are also phosphorescent. This proof may possibly be furnished when a still greater velocity can be given to the wheels of the phosphoroscope.

*Theory of Fluorescence.*—As a fluorescent body is capable of converting perfectly homogeneous light into rays of different refrangibilities, the phenomenon of fluorescence seems to be somewhat analogous to that of incandescence; and as the nature of incandescence is independent of the molecular constitution of the ignited body, the latter problem, as the more simple one, will probably have to be solved before a general theory of fluorescence can be given. So much only may be said at present, that no theory can be accepted which would be at variance with Stokes's law.

R. S.

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### Spectrum of the Aurora Borealis. By H. C. VOGEL (Pogg. Ann., cxlvi, 569—585).

THE author has used an eleven-inch equatorial with an appropriate star spectroscope, furnished with a direct vision-prism made up of five prisms, with a refracting angle of  $90^\circ$ . About 100 lines of the solar spectrum were measured in the instrument, to allow any new lines observed to be easily reduced to wave-length measurements. The author gives his observations and measurements of lines taken on five occasions from October, 1870, to April, 1871. In order to compare the lines observed with those of terrestrial bodies, he has examined the spectra of oxygen, hydrogen, nitrogen, and of atmospheric air in Geissler's tubes; he does not, however, appear to have examined these gases under different conditions of pressure and temperature, but only the spectra obtained in different parts of the same tube. The wave-lengths of the various lines have been calculated, and are given in detail. The author's observations lend a considerable support to the view that the spectrum of the aurora borealis is a modification of the air spectrum. A comparison of some of the lines observed in auroræ with the lines of iron, show a tolerable coincidence, with the exception that the relative intensities of the lines in the two spectra are not the same. The author thinks that if it could be shown that the lines of iron could be made to assume the relative brightness of the lines observed in auroræ by a change of temperature or pressure, the coincidence would be almost sufficient to prove the existence of iron in the stratum of our atmosphere where auroræ take place.

A. P.



**Researches on the Temperature of Solidification of Saline Solutions.** By L. DE COPPET (Ann. Chim. Phys. [4], xxiii, 366— and 502—553).

I. *A. Historical Review of former Researches on this subject.*

II. *Temperature of Solidification of so-called Supersaturated Saline Solutions.*—Rüdorff considers the ice which is separated on throwing a fragment of ice into a supersaturated solution of sodium sulphate, as pure ice, on the ground that the smallest quantity of solidified sodium sulphate contained in it could not have failed to cause the precipitation of the whole salt in solution. The author, however, thinks it possible that the ice separated in this experiment may contain crystals of  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ , which would not, like the ten-atom salt, provoke the crystallisation of the dissolved sodium sulphate; it remains, therefore, still an open question, whether in the solidification of a saline solution we have a complete separation of the solvent from the salt. Whilst the quotient  $\frac{C}{M}$ , where C denotes the decrease of the freezing temperature produced by the addition of M parts of salt to 100 parts of water, is, according to Rüdorff, either constant or increasing with increasing M, the author has found that in some cases  $\frac{C}{M}$  decreases with increasing M. How this quotient, by its constancy or its change for different values of M may serve as a clue to the state of hydration of the salt in solution, has been shown in the abstract of a paper by Rüdorff (see this *Journal*, p. 781, 1872).

III. *Decrease of the Temperature of Maximum Density of Saline Solutions below  $+4^\circ\text{C}$ .*—This decrease being denoted by D, it was found that the state of hydration of a salt in solution can as well be inferred from the changes of the quotient  $\frac{D}{M}$  as from those of  $\frac{C}{M}$ .

IV. *Dissociation of Hydrated Salts in Aqueous Solution.*—The author believes that a tendency to dissociation, favoured by increase of temperature, exists in aqueous solutions of salts, as well as in the solid hydrates. Assuming this, he comes to the following conclusions:—  
1. Of two solutions of the same salt, of different concentration, but of equal temperature, the one which is less concentrated may contain an equal or a greater, but never a smaller proportion of the hydrated salt.  
2. If two solutions of the same salt, of different concentration, but of equal temperature, contain the salt in a state of partial decomposition, the less concentrated always contains the greatest proportion of the hydrate.

For every salt capable of forming two or more hydrates two temperatures must exist, between which its solution contains a mixture of the two hydrates, whilst either above or below these temperatures only one hydrate is present.

V. *Interpretation of the Experiments on the Temperature of Solidification and of Maximum Density of Saline Solutions, with regard to their Chemical Constitution.*—For calculating the number of molecules of water

with which a salt, anhydrous or hydrated, combines on being dissolved in water, and which is called  $r$ , the following formula is given :

$$r = \frac{100(A + 18n)}{18} \times \frac{M'_nC'' - M''nC'}{M'_nM''_n(C'' - C')}$$

in which  $M'_n$  and  $M''_n$  signify two different quantities of salt combined with  $n$  molecules of water of hydration ( $n$  may be  $= 0$ ) dissolved in 100 parts of water.  $C'$  and  $C''$  denote corresponding freezing points, and  $A$  the molecular weight of the anhydrous salt. It is shown that although two observations of  $C$  for two different values of  $M$  will give a probably true value of  $r$ , more observations and various considerations are required for controlling it, the main proof of the correctness of  $r$  being that it remains constant for different values of  $M$ . If it should vary, another hydrate with  $n + s$  atoms of water is likely to have been formed.

The values furnished by the above formula will be denoted by  $\rho$  as long as they have not been controlled. When  $r$  has been determined,  $h_{n+r}$ , i.e., the decrease of the freezing temperature caused by the addition of one part of the  $n$ -atom salt to 100 parts of water, and also  $H_{n+r}$ , i.e., the decrease of the freezing temperature caused by the addition of the atomic proportion of the  $n$ -atom salt to 100 parts of water can be calculated. Between  $h_{n+r}$  the coefficient of the decrease (*coefficient de l'abaissement*), and  $H_{n+r}$ , the atomic decrease (*abaissement atomique*), the following relation exists :—

$$H_{n+r} = [A + 18(n+r)]h_{n+r}.$$

VI. *Experiments on the Freezing Temperature.*—The highest temperature at which solidification was started by a fragment of ice being thrown into the solution, was always taken as  $C$ . The flask containing the solution was generally placed in a mixture of water and alcohol, which was surrounded by a freezing mixture; some cotton-wool in the neck kept the inside protected from particles of dust. Every experiment in which the solidification of the salt commenced before that of the water, was rejected.

VII. *Chemical Constitution of several Saline Solutions according to Observations on their Temperatures of Freezing and of Maximum Density.*—The letters used in this paragraph have the same meaning as before;  $t$  denotes the temperature of maximum density, that of water being taken  $= 4^\circ \text{C.}$ ; ( $c$ ) and ( $d$ ) placed above  $h$  and  $H$ , refer respectively to the temperature of freezing and of maximum density; the letters  $n$ ,  $r$ ,  $s$ , and the numbers 1, 2, 3, &c., placed below  $h$  and  $H$ , express the state of hydration of the salt in question,  $n$  = the number of atoms of water present in the solid salt,  $r$  = the number of additional atoms of water with which the salt combines on dissolving in water. It is to be remarked that in the case of several salts only a probable, but by no means decisive result could be arrived at with regard to the values of  $r$  and  $H_{n+r}$ .

*Chloride, bromide, and iodide of potassium.*  $H^{(c)} = 33.6$  for KCl,  $H^{(c)} = 34.8$  for KBr,  $H^{(c)} = 35.2$  for KI.  $r = 0$  for the three salts.

*Bromide and Iodide of Sodium.*—The quotient  $\frac{C}{M_3}$  being more constant than  $\frac{C}{M_4}$ , it appears that these salts are dissolved, not as NaBr, 4H<sub>2</sub>O and NaI.4H<sub>2</sub>O, as Rüdorff thinks, but as NaBr.3H<sub>2</sub>O and NaI.3H<sub>2</sub>O. From this follows  $H_3^{(c)} = 33.9$  for NaBr.3H<sub>2</sub>O and  $H_3^{(c)} = 34.7$  for NaI.3H<sub>2</sub>O. Therefore, *the atomic decrease of the freezing temperature is very nearly the same, not only for the trihydrated bromide and iodide of sodium, but also for the chloride, bromide, and iodide of potassium; and as it can be shown that the atomic decrease of the higher hydrate of a certain salt must be greater than, or equal to the atomic decrease of the lower hydrate, it appears likely that the atomic decrease of the freezing temperature is very nearly the same for the different hydrates of the same salt.*

*Sodium Chloride.*—The ratios  $\frac{C}{M}$  or  $\frac{D}{M}$ , increase whatever supposition may be made about the state of hydration; we must therefore conclude that the solution of sodium chloride, at its temperature of solidification and of maximum density, contains a mixture either of the anhydrous salt and a hydrate, or of two hydrates.

In the case of a mixture the true formula cannot be determined. The values of  $H^{(c)}$  have been calculated for the compounds which are the most probable to exist in solution, namely, NaCl.2H<sub>2</sub>O and NaCl.3H<sub>2</sub>O. These values,  $H_3^{(c)} = 31.4$  and  $H_2^{(d)} = 33.8$ , do not differ much from those of the allied salts. There is besides  $H_3^{(d)} = 146.7$  for  $M = 7.43$  and  $H_3^{(d)} = 139.7$  for  $M = 8$ .

It can be shown that the ratio  $\frac{H_n^{(d)}}{H_n^{(c)}}$  must be the same for every value of  $n$ , and that it must be equal to the ratio  $\frac{C}{D}$  for that solution, for which the temperature of freezing and of maximum density are equal. The value of  $M$  corresponding to this solution is denoted by  $\mu$  and its temperature of freezing (D) by  $\tau$ ;  $\rho$ ,  $\tau$ , and  $\mu$  can be determined by finding the point of intersection of two curves obtained by raising the numerical values of  $C$  and  $D$  as verticals from a straight line along which the corresponding values of  $M$  are reckoned as abscissæ. For sodium chloride  $\mu$  is  $= 2.32$  and  $\tau = -1.32$  and  $\frac{H_n^{(d)}}{H_n^{(c)}} = \frac{\tau - 4}{\tau} = 4.03$ .

*Ammonium Chloride.*—The ratio  $\frac{C}{M}$  is constant, according to Rüdorff's experiments, whilst the author finds that it increases slightly, at least from  $M = 10$ . Admitting  $r = 0$  for dilute solutions,  $H^{(c)}$  would be  $= 34.8$ , which differs very little from the value of  $H^{(c)}$  of the other salts in this group.

*Calcium Chloride.*— $\rho$  lies between 14 and 16, for  $M = 3.71$ ; from which we may infer the existence of the hydrate CaCl<sub>2</sub>.15H<sub>2</sub>O in solu-



tion.  $H_{15}^{(c)}$  is  $= 43.2$ ,  $H_{15}^{(d)} = 175$ , and  $\frac{H_{15}^{(d)}}{H_{15}^{(c)}} = 4.05$ ,  $\mu = 3.00$ ,  $\tau = -1.31^\circ$ .

The existence of a hydrate containing more atoms of water than the ordinary salt,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , seems to be confirmed by the fact that a fragment of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , thrown into a solution of calcium chloride at zero, does not provoke crystallisation of the salt, whilst it would do so at the ordinary temperature.

It is noteworthy that the solutions of sodium chloride and of calcium chloride, which freeze at the temperature of their maximum density, have nearly the same temperature of solidification and of maximum density.

*Strontium Chloride.*—Its solution seems to contain a mixture of  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  and of a higher hydrate, or of two hydrates with more than 6 atoms of  $\text{H}_2\text{O}$ . Supposing that  $r = 15$ , then  $H_{15}^{(c)}$  would be  $\approx 41.6$ .

*Barium Chloride.*—For  $M \approx 20$ , the ratio  $\frac{C}{M_2}$  is very nearly constant, but it increases for  $M_2 > 20$ . Supposing the hydrate  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  to be formed for  $M_2 \approx 20$ , then  $H_2^c = 46.9$ . If, however,  $\text{BaCl}_2 \cdot 15\text{H}_2\text{O}$  should be formed, then  $H_{15}^{(c)} \approx 43.4$ .

*Manganese Chloride.*—The constancy of the ratio  $\frac{C}{M_{12}}$  which is exhibited in Rüdorff's experiments, seems to prove the existence of the hydrate  $\text{MnCl}_2 \cdot 12\text{H}_2\text{O}$ .  $H_{12}^{(c)}$  would be  $= 47.2$ .

*Cupric Chloride.*—Its blue solution contains  $\text{CuCl}_2 \cdot 12\text{H}_2\text{O}$ ;  $H_{12}^{(c)} = 44.5$ . The green solutions seem to contain a mixture of two hydrates and not  $\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$ , as was supposed by Rüdorff.

*Potassium Carbonate.*—The ratios  $\frac{C}{M_6}$  and  $\frac{D}{M_6}$  being constant for  $M20$ ,  $M_6$ , the solution  $M \approx 20$  probably contains the hydrate  $\text{K}_2\text{CO}_3 \cdot 6\text{H}_2\text{O}$ .  $H_6^{(c)}$  is  $\approx 39.6$  and  $H_6^{(d)} = 287$ .  $\frac{H_6^{(d)}}{H_6^{(c)}} = 7.25$ , from which  $\tau = -0.64$  and  $\mu = 2.17$ .

*Sulphates of Magnesium, Zinc, and Iron.*—Between  $0^\circ$  and  $-3^\circ$  these salts seem to be combined in solution with 7 atoms of water. The values of  $H_7^{(c)}$  would be 18 for  $\text{Mg}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ , 15.8 for  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , and 15.3 for  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . For  $C > 3$ , the ratio  $\frac{C}{M_7}$  increases in the case of the sulphates of magnesium and of zinc, thus indicating the formation of higher hydrates, probably of 12-atom salts.

*Cupric sulphate* seems, for temperatures above  $-3^\circ$ , to be dissolved as  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .  $H_5^c = 17.5$ ;  $\frac{H_5^{(d)}}{H_5^{(c)}} = 11.3$ ;  $\tau = -0.39^\circ$ ;  $\mu = 3.49$ .

*Sulphates of Potassium and of Ammonium and Chromate of Potassium.*—The ratios  $\frac{C}{M}$  and  $\frac{D}{M}$  are constant for the sulphate and the

chromate of potassium.  $\frac{C}{M}$  is constant for  $M \leq 30$  for ammonium sulphate. For  $K_2SO_4$  there is  $H^d = 292$ ,  $H^{(c)} = 35$ ,  $\frac{H^{(d)}}{H^{(c)}} = 8.34$ ,  $\tau = -0.55^\circ$ ,  $\mu = 2.74$ , and according to another set of observations,  $H^{(c)} = 39$ ,  $\frac{H^{(d)}}{H^{(c)}} = 7.49$ ,  $\tau = -0.62^\circ$ ,  $\mu = 2.77$ .

If ammonium sulphate exists as such in aqueous solution below  $-11^\circ$ , it must be in a state of hydration; but above this temperature it does not combine with water, as the ratio  $\frac{C}{M}$  is constant.  $H^{(c)}$  is = 36.4 for  $(NH_4)_2SO_4$  and = 38.1 for  $K_2CrO_4$ .

*Potassium Nitrate* exists in solution as  $KNO_3$ ;  $H^{(c)} = 27$ .

*Sodium Sulphate*.—A solution of this salt containing 20 parts of it in 100 parts of water is supersaturated, not only with  $Na_2SO_4.10H_2O$ , but also with the more soluble hydrate,  $Na_2SO_4.7H_2O$ , of which two hydrates, sometimes the one sometimes the other, separates before the formation of ice. The ratios,  $\frac{C}{M}$  and  $\frac{D}{M}$  decrease with increasing  $M$ , a fact which can be explained by assuming that the solution contains a mixture of two different hydrates whose proportions vary with the degree of concentration. It is noticeable that the values of  $H^{(c)}$ , corresponding to these two hydrates are different, whatever supposition may be made about their state of hydration, whilst the value of  $H^{(c)}$  is generally found to be the same for salts of the same group even in different degrees of hydration.

The author thinks that *sodium sulphate*, on dissolving in water, is itself partially modified by the action of the water or the variation of temperature, although we have at present no clue to the nature of this change.  $\mu$  is = 2.04 and  $\tau = -0.57^\circ$ .

*Nitrates of Barium, Strontium, Calcium, and Lead*.—The ratio  $\frac{C}{M}$  decreases for  $Ba(NO_3)_2$ ,  $Sr(NO_3)_2$ , and  $Pb(NO_3)_2$ . According to Rüdorff's experiments, it seems that  $\frac{C}{M}$  is constant for  $Ca(NO_3)_2$ , whilst the author, who made some experiments on more concentrated solutions than those examined by Rüdorff, concludes that  $\frac{C}{M}$  is a variable quantity.

*Potassium Hydrate*.—Its solution, which already at the ordinary temperature deposits crystals of  $KHO.2H_2O$ , contains probably two hydrates, the lowest of them containing not less than two atoms of water. The values  $H_2^{(c)} \leq 33.9$ , and  $H_2^{(c)} \leq 142$ , do not differ from those found for the alkaline chlorides, bromides, and iodides;  $\mu = 2.04$ ,  $\tau = 1.30$ ,  $\frac{H_n^{(d)}}{H_n^{(c)}} = 4.08$ .

*Sodium Hydrate* is in solution probably in the form of the two hydrates,  $2NaHO_3.H_2O$  and  $2NaHO.7H_2O$ . The atomic decrease of the

freezing point is very nearly the same for the hydrates of potassium and of sodium, as  $H_{3\frac{1}{2}}^{(d)} \approx 31.0$ , and  $H_{1\frac{1}{2}}^{(c)} \approx 34.1$ .

*Ammonia* seems to be present in solution as  $NH_4HO$ . The atomic decrease  $H^{(c)} = 19.0$ , being very different from that of the hydrates of potassium and sodium, it may be inferred that *the solution of ammonia has not the same constitution as the hydrates of potassium and sodium.*

R. S.

**Change in Volume of Gases by Pressure.** By MENDELEJEFF  
(Deut. Chem. Ges. Ber., v, 332).

REGNAULT has found that all gases, with the exception of hydrogen, are condensed more by pressure than Mariotte's law requires. If, however this were correct for every pressure, it would be possible to make unliquifiable gases, such as oxygen and nitrogen, denser than water by the pressures at our command. The atomic weights of these elements show, on the contrary, that they must possess, when in the liquid state, densities less than that of water. It may therefore be surmised that at high pressures the contraction of gases is less than that required by Mariotte's law. This view is confirmed by the experiments and observations of Rumford and Rodman, and by those of Natterer. These considerations lead us to conclude that there is an intermediate state in which Mariotte's law obtains. This state should be, according to the author, at a pressure of about 53 atmospheres.

In order to set at rest a matter of such importance, the author has undertaken a series of investigations on the condensation of gases by pressure. He believes that he will be able to employ a manometer for pressures as high as 150 atmospheres; and in order to avoid the errors arising from surface-condensation, he intends to employ a gravimetric method instead of that which has been hitherto adopted.

T. B.

**A new Water Air-pump.** By G. JAGNO (Deut. Chem. Ges. Ber., v, 328).

THIS pump consists of a —| shaped piece of glass tube 8 or 10 millimeters in diameter. To its horizontal branch, which is about 2 inches long, is joined a small tube, one end of which is connected with the vessel to be exhausted, the other end terminating inside the horizontal branch, and being provided with a Bunsen's caoutchouc valve opening therein. The upper end of the vertical tube is cut off obliquely, and connected with the water supply by means of an india-rubber tube of equal diameter, and long enough to hang down and close the top of the glass tube. The lower part of the vertical tube, out of which the water flows, is from half a meter to a meter in length. If a receiver be now connected with the exhaustion-tube, and the water be allowed to flow through the apparatus, the india-rubber tube begins to pulsate, alternately closing and opening the top of the vertical tube, a powerful suction taking place at the same time through the Bunsen's



valve. With an inflow and outflow of about one meter, an exhaustion of 700 millimeters was obtained. This apparatus obviously depends on the same principle as the hydraulic ram, the india-rubber tube taking the place of the valves of that engine.

T. B.

**Researches on Crystalline Dissociation: the Alums.** By P. A. FAVRE and C. A. VALSON (*Compt. rend.*, lxxv, 798—803).

THIS portion of the authors' memoir contains the results of their determinations of the variation in volume caused by the solution of the various alums. These were obtained by two methods—first by a comparison of the density of the salts and of the solutions; secondly, by observing the increase of volume caused by the solution of a known weight of the salt in a determinate quantity of water, contained in a reservoir surmounted by a narrow calibrated tube. The two tables which accompany the communication give the experimental and calculated results, from which the authors infer that the desiccated alums cannot be regarded as simple mixtures of their constituent salts. This is confirmed by the behaviour of ammonia-alum when desiccated; for it does not lose ammonia, even at a temperature which is sufficient to entirely volatilize ammonium sulphate.

It would seem that the constituent salts in desiccated alums remain more or less combined, although the density of dehydrated ammonium alum is sensibly equal to that which it should have if it were a simple mixture of its constituent salts, and in the case of potassium alum it is even less than the calculated number.

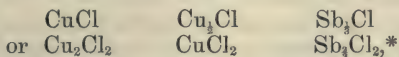
C. E. G.

**An attempt to determine the Molecular Weights of Saline Substances.** By E. PATERNÒ (*Gazzetta Chimica Italiana*, ii, 245—253).

It is well known that great uncertainty exists respecting the molecular weights of compounds whose vapour-densities cannot be experimentally determined, either because they are not volatile, or because their vapours when raised to high temperatures undergo decomposition or dissociation. Thus it is not yet known with certainty whether the molecules of cuprous, mercurous, and stannous chloride should be represented by the formulæ  $\text{CuCl}$ ,  $\text{HgCl}$ , and  $\text{SnCl}_2$ , or by  $\text{Cu}_2\text{Cl}_2$ ,  $\text{Hg}_2\text{Cl}_2$ , and  $\text{Sn}_2\text{Cl}_4$ ; and whether the ferrous, chromous and manganous salts of monobasic acids should be represented by formulæ containing 1 or 2 atoms of metal, whether, for example, the molecule of ferrous nitrate contains  $\text{Fe}(\text{NO}_3)_2$  or  $\text{Fe}_2(\text{NO}_3)_4$ .

These considerations show the importance of seeking for a method of determining molecular weights independent of the vapour-densities and capable of general application. Such a method, the author of this paper believes may be found in the determination of the weights of different compounds which are decomposed under the influence of the same electric current.

Faraday, from his classical experiments on electrolysis, inferred that the weights of elements separated by the same electric current passing through various electrolytes are to one another in the proportion of their chemical equivalents. This law was deduced by Faraday from the electrolysis of a number of compounds of very simple constitution, which were supposed to contain "equal equivalents" (equal numbers of atoms) of their respective elements (e.g.,  $\text{HO}$ ,  $\text{HCl}$ ,  $\text{SnCl}$ ,  $\text{PbCl}$ , according to the atomic weights then adopted); and it was afterwards extended to more complex compounds by Matteucci (*Bibliothèque universelle de Genève*, xxi, 1839), and Becquerel (*Ann. Chim. Phys.* [3], xi, 102, 257), whose experiments showed that when an electric current decomposes simultaneously a number of compounds containing 1 equivalent of an element combined respectively with 1, 2 and 3 equivalents of another element (for example, the two chlorides of copper, and trichloride of antimony), the chemical actions on the three compounds, measured by the quantities of the [metallic] element separated, are as the numbers 1,  $\frac{1}{2}$ ,  $\frac{1}{3}$ ; in other words, the relative quantities of the three compounds decomposed by the same current are represented by the formulæ:—



the same quantity of chlorine being separated in a given time from each of the three compounds.

Further, it is known that water and oxygenated water (hydrogen dioxide) when decomposed by the same current, yield at the negative pole equal quantities of hydrogen, and at the positive pole quantities of oxygen which are to one another as 1 : 2; in other words, that the current which decomposes  $\text{H}_2\text{O}$  is necessary and sufficient to decompose  $\text{H}_2\text{O}_2$ . In like manner it is found that when water and the two chlorides of copper are simultaneously electrolysed, for every 1 pt. of hydrogen given off from the water (in a voltameter, for example), 31.5 pts. of copper are separated from the cupric, and 63 from the cuprous chloride,—that is to say, the quantities of the three compounds simultaneously decomposed are  $\text{H}_2\text{O}$ ,  $\text{CuCl}_2$  and  $\text{Cu}_2\text{Cl}_2$ . A similar result is obtained by the simultaneous electrolysis of the two oxides of copper in ammoniacal solution, or of cuprous thiosulphate,  $\text{Cu}_2\text{S}_2\text{O}_3$ , and cupric sulphate,  $\text{CuSO}_4$ , the cuprous compound in each case yielding twice as much copper as the cupric compound (Becquerel, *Ann. Chim. Phys.* [3], xi, 177—180).

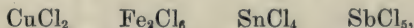
It appears then, that the same current that decomposes a molecule of water,  $\text{H}_2\text{O}$ , is necessary and sufficient to decompose  $\text{H}_2\text{O}_2$ ,  $\text{CuCl}_2$ ,  $\text{Cu}_2\text{Cl}_2$ ,  $\text{CuO}$ ,  $\text{Cu}_2\text{O}$ , &c.; and as the quantities thus represented are usually regarded as the molecules of the several compounds, the author of this paper thinks himself warranted in drawing the general conclusion, that an electric current which successively traverses different electro-

\* This result may be expressed in the words of Faraday's law, viz., that the quantities of the several elements are represented by their chemical equivalents, the equivalent of copper being 63 in the cuprous compounds,  $\frac{63}{2}$  in the cupric compounds, and that of antimony  $\frac{1}{3} \times 123$ , or  $40\frac{1}{3}$  in antimonious chloride, the equivalents being the quantities of the metals which unite with 35.5 parts of chlorine, or may be supposed to replace 1 part of hydrogen.



lytes, decomposes in each an equal number of molecules; or, the current capable of decomposing a molecule of water is necessary and sufficient to decompose a molecule of any other chemical compound.

The law thus generalised is, however, entirely at variance with Faraday's law of equivalent electrolytic decomposition, as extended by Matteucci and Becquerel; for it would lead to the inference that when cupric, ferric, stannic, and antimonious chlorides are simultaneously electrolysed, the quantities decomposed in the same time would be those represented by the formulæ—



whereas, according to Matteucci and Becquerel, they should be—



the same quantity of chlorine being evolved in each case.

The author doubts the conclusiveness of Becquerel's experiments, but admits, at the same time, that he is not yet in possession of the experimental data necessary to establish his own view. He states, however, his intention of pursuing the subject further, and, in the mean time, points out certain consequences which would follow from his law of electrolysis if established, viz.:—

1. The molecule of stannous chloride contains  $\text{SnCl}_2$ , not  $\text{Sn}_2\text{Cl}_4$ , inasmuch as Faraday has shown that 59 parts of tin are separated by electrolysis for every 1 pt. of hydrogen evolved from water, or  $\text{SnCl}_2$  for  $\text{H}_2\text{O}$ .

2. The molecules of the cuprous and mercurous compounds contain 2 atoms of metal.

3. The molecules of the argentic salts, and of the salts of the alkali-metals contain 2 atoms of metal, since 108 pts. of silver, 23 of sodium, &c., are eliminated by the current for every 1 pt. of hydrogen; or, the current which decomposes  $\text{H}_2\text{O}$ , decomposes also  $\text{Ag}_2(\text{NO}_3)_2$ ,  $\text{Ag}_2\text{SO}_4$ ,  $\text{K}_2\text{Cl}_2$ ,  $\text{K}_2(\text{HO})_2$ , &c.

4. When an aqueous halogen-acid ( $\text{HCl}$ ,  $\text{HI}$ , &c.) is decomposed by the current, the real electrolyte is not the hydracid, as generally supposed, but the water, inasmuch as the current which decomposes  $\text{H}_2\text{O}$ , decomposes also  $\text{H}_2\text{Cl}_2$ ,  $\text{H}_2\text{I}_2$ , &c., whereas the vapour-densities of these acids show that their molecules are  $\text{HCl}$ ,  $\text{HI}$ , &c. This the author explains by supposing that the current decomposes the water in which the acid is dissolved, and that each atom of oxygen thereby transferred to the positive pole decomposes 2 molecules of hydrochloric acid, &c., forming  $\text{H}_2\text{O}$  and eliminating  $\text{Cl}_2$ , &c. This view, as the author mentions, is at variance with the recent experiments of Bourgoin (*Bull. Soc. Chim. de Paris* [2], xvii, 242) on the electrolysis of aqueous sulphuric, nitric, and oxalic acid, from which it seems to follow that water is not an electrolyte at all—a conclusion quite in accordance with the well-known experiments of Davy, which showed that pure water when kept from contact with all substances from which it can derive any saline constituents, is absolutely incapable of conducting the current, even of a very powerful battery.

On the whole then, it appears that the views advanced by the author



in this paper, and especially the assertion that an electric current traversing a number of electrolytes always decomposes an equal number of molecules in each, are at variance with laws hitherto regarded as well established, and cannot, therefore, be received as true without further and decisive experimental evidence.

H. W.

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*Constitution of Liquids.* By A. HANDL (Wien. Akad. Anzeige, 1872, 88; Chem. Centr., 1872, 433).

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*Spectroscopic Researches on the Sun.* By P. SECCHI (Compt. rend., lxxv, 749).

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## Inorganic Chemistry.

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**A simple Apparatus for the Production of Ozone with Electricity of High Tension.** By A. W. WRIGHT (Am. J. of Sci. [3], iv, 26, and Chem. News, xxvi, 113).

THE author's modification of the apparatus usually employed for the production of ozone by means of the silent discharge is thus described.

A straight glass tube, about 20 centimeters long and 2.5 centimeters in diameter, is closed at both ends with varnished corks. Through the axis of each cork is inserted a glass tube of about 5 mm. calibre and 7 centimeters in length, having a branch tube inserted perpendicularly at the middle. The outer ends of the tubes are closely stopped with corks, and a straight thick copper wire passed through each. The inner extremity of one of these wires carries a small ball; the other terminates in a disc with rounded edge, set perpendicularly to the axis of the tube, and so large as to leave an annular space of 2 or 3 mm. breadth around it. Air or oxygen is admitted through one of the branch tubes, and allowed to escape from the other, after having passed through the whole length of the tube.

In using the apparatus, the wires must be connected with the poles of the machine in such a manner that the disc becomes the negative terminal, since this arrangement gives the greatest degree of expansion and diffuseness to the current. The ball and disc must be adjusted to a proper distance, and the current of gas caused to pass from the negative towards the positive extremity of the tube. On setting the machine in motion, ozone is rapidly produced, and in great quantity.

The efficiency of the apparatus was judged by noting the rapidity with which the gas, after passing through the ozonising tube, bleached a solution of indigo, or decomposed a solution of potassium iodide; but no direct determination of the percentage of ozone produced was made.

It was noticed as a fact that the effects were much more rapid and

energetic with oxygen than with air, and that in the former case, in order to destroy the direct spark, it was necessary to separate the terminals to a much greater distance from each other.

J. W.

### Action of Ozone upon Vulcanized Caoutchouc. By A. W.

WRIGHT (Am. J. of Sci. [3], iv, 29).

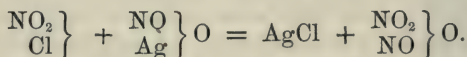
It was noticed that the ebonite insulators belonging to Holtz's electro-machine, and the ebonite jackets of some induction-coils became unusually hygroscopic soon after the instruments had been used for the production of ozone, to such an extent, indeed, that the accumulated liquid was sometimes so abundant as to trickle down in drops. An examination of this liquid showed that it contained a considerable amount of free sulphuric acid, the presence of which was attributed to the action of the ozone upon the sulphur of the vulcanized caoutchouc. Experiments were made which confirmed this supposition. Air, strongly ozonized, was passed through a vulcanized rubber tube, and then bubbled through water. In a short time the water acquired the odour of sulphurous oxide, and ultimately gave a white precipitate with barium chloride.

In a similar manner a thin dry slip of ebonite placed in a small bottle into which ozone was driven, became in a short time bedewed with moisture having an acid reaction, and exhibiting the same properties as that found on the insulators of the machine. An attempt to oxidize free sulphur by means of ozone was unsuccessful.

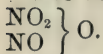
J. W.

### Synthesis of Nitrogen Tetroxide. By A. EXNER (Chem. Centr., 1872, 273).

THE synthesis was effected by the action of nitril chloride on silver nitrite—



The reaction tends to establish for nitrogen tetroxide the formula



H. W.

### Nitric Anhydride and a New Nitric Hydrate. By RUDOLPH WEBER (Pogg. Ann., cxlvii, 113—128).

THE attempts hitherto made to dehydrate nitric acid by means of phosphoric anhydride have not succeeded, in consequence of the decomposition of the nitric anhydride. The author has succeeded in doing so by adopting the following process:—The most concentrated nitric acid freed from nitrous acid as much as possible, and cooled by ice, is treated with phosphoric anhydride, which, as it acts upon it very violently at first, is added slowly and in small quantities at a time. The syrupy product is distilled so long as anything comes over at a blood-heat, and condenses in oily drops in the neck of the retort; the two layers of liquid, of which the distillate is found to consist, are separated by decan-

tation, the lower layer being an impure new nitric hydrate. The upper layer, which consists of nitric anhydride, nitrous acid, and some hydrate, is cooled by ice-water, which renders it turbid, and causes a small quantity of a clear, coloured liquid to separate. This liquid, which consists of nitric anhydride and nitrous acid, is further cooled by ice or a freezing-mixture, when some of the nitric anhydride crystallises in well-formed, transparent, yellowish prisms, leaving a liquid compound of nitric anhydride and nitrous acid, which appears to be richer in the former than nitroso-nitric acid. Lastly, the anhydride is purified by cautiously fusing it, again crystallising it by cold, and draining off the mother-liquor.

The melting point of nitric anhydride thus prepared is about  $30^{\circ}$ . It is very unstable, particularly in the fused state, but can be preserved for several days at  $10^{\circ}$  in a dry atmosphere. It is volatile at ordinary temperatures, and its vapour condenses in beautiful crystals in the cooler part of the tube containing it. In a freezing mixture it is almost colourless. The specific gravity of the solid anhydride exceeds 1.64; that of the liquefied anhydride is less than 1.636.

It acts with great violence upon sulphur, forming a compound of sulphuric anhydride and nitrous acid. It also acts with great energy upon phosphorus, potassium, and sodium, setting them on fire. Upon organic substances it also acts with great intensity. It does not act upon charcoal, but this substance when previously kindled burns with great brilliancy in its vapour. It acts upon zinc, cadmium, mercury, and arsenic, and slightly upon magnesium and thallium, but has no action upon most other metals.

On cooling the lower layer of the distillate from nitric acid and phosphoric anhydride in a freezing mixture, the new nitric hydrate crystallises out. It can also be prepared by adding nitric anhydride to nitric acid. The anhydride dissolves with development of heat until the new hydrate,  $2\text{N}_2\text{O}_5 \cdot \text{H}_2\text{O}$ , is produced, but any further quantity of it remains insoluble. The pure hydrate is obtained by crystallising it out in a freezing mixture, draining it from the mother-liquor, allowing it to melt, and again crystallising it. Both this hydrate and the anhydride have been analysed. In its chemical properties the hydrate resembles the anhydride. It is liquid at ordinary temperatures, but less so than the ordinary hydrate, and more or less yellow-coloured; solid at about  $-5^{\circ}$ . Its specific gravity at  $18^{\circ}$  is 1.642. It slowly decomposes at ordinary temperatures. When heated it partly distils unchanged, but nitric anhydride is also formed, so that the distillate consists of two layers, the upper being the anhydride. In this decomposition it resembles fuming sulphuric acid.

When nitric acid is distilled with fuming sulphuric acid, oxygen, nitrous vapours, and a compound of the composition  $\text{SO}_3\text{N}_2\text{O}_3 \cdot 3\text{SO}_3\text{H}_2\text{O}$  come over.

E. D.

**Behaviour of Iodine with Acids.** By CARL KRAUS (N. Repert. Pharm., xxi, 385—387).

IODINE dissolves in concentrated sulphuric acid, nitric acid, hydrochloric, phosphoric, acetic, tartaric, and citric acids. Some of it crys-



tallises out from its solution in sulphuric acid or nitric acid on standing. The sulphuric and nitric solutions do not react with starch, even when this is present in excess and unchanged, and when water is added—provided the acid is not in too small a quantity. The hydrochloric solution gives the colour with starch, unless large quantities of concentrated acid are present. All the solutions yield the iodine to carbon bisulphide. Concentrated sulphuric acid and nitric acid precipitate some of the iodine from concentrated aqueous or alcoholic solutions of it in potassium iodide.

E. D.

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**Oxidising Power of Potassium Iodate.** By E. SONSTADT  
(*Chemical News*, xxvi, 98).

THE communication on this subject appears to be only a preliminary notice. Some time ago the author met with a carbonaceous mineral, which, while it closely resembled anthracite in appearance, was not sensibly affected when treated with the more commonly employed, and most powerful oxidising agents. But when the powder, or even fragments of the mineral were mixed with potassium iodate, and heated to fusion, deflagration instantly ensued, and the mineral rapidly disappeared by oxidation to carbonic anhydride.

The successful employment of potassium iodate in the above instance, induced the author to try its action upon some other minerals, more especially the sulphides. At present, however, the results are not sufficiently complete to be worth communicating. The energy of potassium iodate as an oxidising agent, as compared with chlorates and nitrates, is attributed to the fact that in the first place it decomposes at a higher temperature than does potassium chlorate; and whereas a nitrate, under similar circumstances, evolves mixed gases, the fused iodate gives off an abundant supply of pure oxygen.

When a solution of an alkaline iodate is mixed with an alkaline thiosulphate, no chemical action ensues as long as the solution remains neutral, but the addition of a small quantity of an acid causes it to become in the first place strongly alkaline; a neutral point is presently reached, after which, if the iodate be in excess, the further addition of acid liberates iodine. The products of the reaction up to neutrality are, of course, a tetrathionate, an iodide, and a salt of the acid used.

When citric or tartaric acid is employed to acidify the mixed solution of iodate and thiosulphate, the solution becomes neutral to test-paper when two molecules of the acid have been added for every six molecules of thiosulphate present, and this neutral point is reached sensibly before iodine is set free. A trisodium salt of the acid is in both instances formed. In order to obtain the iodine reaction, a quarter of a molecule more of citric acid and one molecule more of tartaric acid must be added.

J. W.

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**Lithium Hydrate.** By MURETOW (*Deut. Chem. Ges. Ber.*, v, 331).

AN aqueous solution of lithia evaporated in a vacuum, yielded a hydrate  $\text{LiHO} \cdot \text{H}_2\text{O}$ , which was slightly hygroscopic.

H. W.

**Preparation of Potassium Chlorate.** By W. HUNT (Dingl. Polytech. J., ccv, 77).

DILUTED chlorine gas is passed into a brick tower, into which there also drops a solution of potassium chloride and milk of lime. The potassium chlorate formed is separated by crystallisation.

M. M. P. M.

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**Preparation of Thallium on the Large Scale.** By MAX SCHAFFNER (Dingl. Polytech. J., ccv, 55—57).

THE fine dust obtained in roasting pyrites in the sulphuric acid manufacture at Aussig is the raw material. The process is almost identical with that already known.

M. M. P. M.

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**Preparation of Pure Stannates of the Alkalis.** (Dingl. Polytech. J., ccv, 76.)

TIN filings are treated with caustic potash or soda solution of specific gravity 1.2, the solution run off, and atmospheric air being pumped into it, the solution is again made to act on the tin, and so on, until a sufficient quantity of the desired salts is obtained. If the solution be gently warmed, and warm air be used, the process is more speedy.

M. M. P. M.

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**Didymium in British Minerals.** By A. H. CHURCH (Chemical News, xxvi, 130).

DIDYMIUM has been found in cryptolite, and as the latter has been found to occur in both British and foreign specimens of apatite, this may be considered as being equivalent to the detection of didymium in the last-named mineral.

J. B.

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**The Fusion of Metallic Arsenic.** By J. W. MALLET (Chemical News, xxvi, 97).

THE following experiments were undertaken in order to verify or disprove the statement, that arsenic cannot be fused, but passes directly from the solid into the vaporous state. Arsenic, in the form of coarse powder, was placed in a thick barometer-tube of soft glass and of small bore, well sealed at both ends, and enclosed in a piece of wrought-iron gas-tubing, closed at each end by an iron screw-cap; the space between the two tubes was filled with sand, and the whole was heated to redness by a charcoal fire.

A similar iron tube placed beside the former served to contain several little glass tubes with samples of different metals, whose fusion might afford some indication of the temperature at which that of the arsenic occurred.

Arsenic thus treated was found on cooling to have fused into a perfectly compact crystalline mass, moulded to the shape of the tube, of

steel-grey colour and brilliant lustre; sp. gr. 5.709 at 19°. It possessed a considerable degree of cohesive strength as compared with common sublimed arsenic, and even seemed to exhibit faint traces of flattening before crushing under the hammer. The temperature required for fusion lay between the melting points of antimony and silver.

J. W.

**The Metallurgy of Manganese.** By HUGO TAMM (Chemical News, xxvi, 111).

THE author has practically studied the smelting of manganese ores upon a manufacturing scale, and has succeeded in obtaining refined manganese containing 99.9 per cent. of metal.

The following is an outline of the plan adopted for the reduction of the ore:—

*Fluxes.*—Two fluxes are required. No. 1, or white flux, is prepared by mixing together ground glass 63 parts, quicklime  $18\frac{1}{2}$  parts, fluor spar  $18\frac{1}{2}$  parts. It is a fusible flux, and is principally required for the preparation of No. 2, or green flux.

The latter is made by smelting together: Flux No. 1, 34 parts; lamp-black or soot,  $5\frac{1}{2}$  parts; manganese dioxide, of good quality,  $60\frac{1}{2}$  parts. The slag obtained in this operation alone is required. It presents a fine green colour from the presence of manganates, and when once prepared may be used over and over again, provided the manganese ore reduced is of tolerably good quality. It requires from time to time the addition of a little white flux to improve its fusibility.

*Crucibles.*—On account of the high temperature required for the reduction of manganese, some difficulty was experienced in obtaining a crucible which would withstand the action of the molten flux. The following remedy was finally devised:—The interior of the crucible is lined with a paste, made by mixing 3 parts of plumbago and 1 part of loam or fire-clay with a small quantity of water. This lining, which should not under any circumstances exceed half an inch in thickness, effectually protects the crucible.

*Smelting the Ore.*—The following proportions are recommended:—

Manganese dioxide, of good quality . . . . .	1000	parts
Lamp-black or soot, of good quality . . . . .	91	„
Green flux . . . . .	635	„
Oil in sufficient quantity to wet the mixture.		

The mixture is introduced into a crucible prepared as above directed, and a cover of thick wood placed over it. The latter is carbonised during the smelting, but forms a charcoal cover which protects the mixture from oxidation. A clay cover is subsequently luted over the whole. The crucible is then placed in a wind-furnace, and slowly heated as long as fumes escape; the fire is then urged, and the crucible maintained at a white heat for several hours; the time actually required depending upon the quantity operated on.

When cold, the contents of the crucible are turned out, the button of metal detached from the slag, and preserved in a well-closed bottle.



*Refining.*—The cast-manganese obtained by smelting an ore containing 79·5 per cent. of manganese peroxide was found to contain manganese 96·9, iron 1·05, with traces of carbon, silicon, and other metals. It may be refined by re-melting it in a close crucible, with one-eighth of its weight of manganese carbonate.

Refined manganese presented the following composition:—

Manganese.	Iron.	Silicon.	Carbon.	
99·91	0·05	0·015	0·025	= 100·0

For the docimastic assaying of manganese ores, experiments should be made on quantities varying from 500 to 1,000 grains of the ore, and the whole operations should be carried out on the small scale exactly as they have been described upon the large scale, without any other modification than that of the reduction of the proportions.

J. W.

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**Metallic Manganese.** By J. E. LOUGHLIN (Chem. News, xxv, 139).

THE specific gravity of metallic manganese prepared by different chemists varies considerably, ranging from 6·85 to 8·015. This probably arises from the metal of lower density containing oxide, since manganese of sp. gr. 7·84, obtained by Gahn's method, which consists in heating the peroxide made into balls with charcoal and oil, showed a sp. gr. of 7·96 when powdered and reheated with charcoal, changing at the same time from a black to a cast-iron colour. Another reheating with charcoal turned it brownish-red and caused a further increase of 0·02. The sp. gr. of other samples of manganese, made by heating the oxide with charcoal and with potassium cyanide and charcoal, also increased to the same point when the metal was reheated with charcoal. The sample first named was raised to 7·993 by a fourth heating with charcoal, with addition of borax. The specific gravity obtained by Deville, 8·015, was not reached by the author.

B. J. G.

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**Certain Reactions of Manganous Chloride.** By F. W. KRECKE (J. pr. Chem. [2], v, 105; Dingl. Polyt. J., cciv, 337).

THE author remarks that on account of the various changes of colour exhibited when manganous chloride solution is evaporated down to certain degrees of concentration, this salt quite as well deserves the name "mineral chameleon" as potassium manganate. On concentrating an aqueous solution of manganous chloride at a temperature from 70° to 100°, the solution, which is at first colourless, becomes rose-coloured, afterwards yellow, and finally, before crystallising, a splendid green.

A solution of rose-coloured crystals of manganous chloride in 10 to 12 parts of water is colourless, either cold or boiling. On evaporating on the water-bath, a little over 70°, and strongly concentrating, the rose colour is developed and gradually increases in intensity, the maximum tint being attained when the solution contains about 15 per

cent. of the salt. By further concentration the rose tint passes into orange, and at last, when 20 per cent. strength is attained, the colour becomes a clear yellow, like that of a solution of potassium chromate. On cooling to below  $70^{\circ}$  the rose tint is regained.

The crystallised manganous chloride dried at  $100^{\circ}$  furnishes a clear green mass, which is not hygroscopic like the original salt. This mass dissolves in water partially, with liberation of heat, yielding a red solution. The undissolved portion is a white powder, soluble in dilute acids, and is a basic salt.

K. J. Bayer (*J. pr. Chem.* [2], v, 445) has repeated the above experiments of Krecke, with perfectly pure manganese salt, and fails to obtain the remarkable changes of colour noticed by the latter. By previously adding small quantities of ferric chloride (red and yellow) or cobalt chloride (blue and green) however to the manganese solution, and then evaporating, these colour-changes made their appearance just as above described. The colour is so characteristic in the case of the cobalt chloride that it may serve very well for the detection of small quantities of cobalt in concentrated manganous chloride solutions.

Bayer remarks that the pure anhydrous manganous chloride is not green, but an easily fusible red body, which solidifies on cooling to a beautiful crystalline mass, possessing a lustre like that of magnesium chloride.

Kolbe gives the following as the simplest method of preparing pure manganous chloride:—"Manganese ore is treated with hydrochloric acid, and the clear filtered solution obtained therefrom is evaporated to dryness, and the residual salt gently ignited in a Hessian crucible in a charcoal furnace. The ignited mass yields on treatment with water a solution of pure manganous chloride absolutely free from iron."

W. S.

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**On Certain Double Salts of Ferrous Sulphate.** By GRAEGER  
(Chem. Centr., 1872, 377).

Most of the double salts of ferrous sulphate coincide in their constitution with the ammonium double salt  $(\text{NH}_4)_2\text{SO}_4 + \text{FeSO}_4 + x\text{H}_2\text{O}$ . The preparation and analyses of these double salts being made for the purpose of ascertaining which would be most suitable for the titration of permanganate solutions, and at the same time for the estimation of the strength of medical chlorine-water, only a limited number of sulphates were experimented with, viz., those likely to exert no disturbing influence in experimenting upon these solutions. The salts prepared were the ammonium, potassium, sodium, magnesium, and zinc double salts.

*Sodio-ferrous Sulphate*,  $\text{Na}_2\text{SO}_4 \cdot \text{FeSO}_4 + 4\text{H}_2\text{O}$ , was prepared by dissolving 1 eq. of pure ferrous sulphate in water, adding 1 eq. of pure sodium sulphate, dissolving and crystallising. It is very easily soluble, so that no crystals can be obtained by cooling a hot concentrated solution; but the crystals are deposited on boiling a concentrated solution, just as in the case of a sodium carbonate solution. This property indicates the existence of a very soluble salt, with a greater amount of water of crystallisation. A concentrated solution of the double salt



allowed to stand for a long time does not deposit crystals, but if it be warmed to  $100^{\circ}$  C. and kept so, the separation of the salt with 4 molecules of water begins to take place. On leaving the solution to evaporate spontaneously, crusts of the salt separate, very hard and difficult to remove from the sides of the dish. The dry salt is a powder-like mass of small crystals, with scarcely a tinge of green. It does not lose weight when heated to  $100^{\circ}$ . Solution of potassium sulphocyanate is unaffected by it. Five closely agreeing determinations gave 27.32 as the average amount of iron contained in 183 parts by weight of the salt. The sodium double salt may be dried at  $100^{\circ}$  without suffering the slightest decomposition, and is then not in the least degree hygroscopic; it thus possesses an undoubted superiority over the ammonium double salt; it also does not effloresce in the air.

*Zinco-ferrous sulphate*:  $\text{ZnSO}_4 \cdot \text{FeSO}_4 + 6\text{H}_2\text{O}$ .—A solution of ferrous sulphate and zinc sulphate is made, containing equal numbers of molecules of the two salts, in as small a quantity of hot water as possible. On cooling, the double salt falls in small, beautiful emerald-green rhombic tables; and on agitating the concentrated solution, it is deposited as a bluish-green powder. It is not hygroscopic, and is not affected by exposure to air. This zinc salt may be used just as well as the preceding for the titration of permanganate solution. In obtaining the crystals of the double salt for this purpose, care must be taken to select only the very small ones; in fact, if a fine sieve be used and the small and large crystals thus obtained be tested, the large crystals will be found to give erroneous results, whilst those obtained with the small ones are correct.

W. S.

**Amount of Combined Water in Crystallised Ammonio-ferrous Sulphate.** By E. FLEISCHER (J. pr. Chem. [2], v, 437—443).

THE author criticises the methods adopted and results obtained by H. Rheineck on the above subject (p. 225 of this volume).

1stly. With reference to the water determination: Rheineck dries the salt at  $110^{\circ}$ , whereby several sources of error creep in, viz., oxidation of the ferrous oxide, removal of small quantities of ammonia by the escaping aqueous vapour, and the possible retention of one molecule of water as water of constitution.

2ndly. The methods of estimating the iron—either by supersaturating the solution of the salt oxidized by nitric acid with ammonia, evaporating and igniting; or by gently igniting a portion of the salt, moistening with ammonia solution, and again igniting till the weight remains constant—are considered open to several objections.

The direct determination of the iron, sulphuric acid and ammonia, and the estimation of the water by difference, is considered on the whole safest and best.

The ammonia was determined by distilling a solution of a known weight of the salt with excess of caustic soda solution into a known volume of acid of ascertained strength. To prevent jumping or frothing over of the contents of the distillation flask, about an equal volume



of strong alcohol was added, and the distillation then progressed without danger. As soon as the alcohol passed over and frothing began, the distillation was stopped. If necessary, the flask may then be placed on the water-bath for some time to expel the last traces of ammonia.

The sulphuric acid was determined in the contents of the distillation flask above mentioned. A known volume of the filtered measured solution was taken and acidified with hydrochloric acid, decomposed by solutions of calcium nitrate and ammonium acetate, and heated to boiling. In the filtered solution the sulphuric acid was determined volumetrically by adding a normal barium chloride solution in slight excess, boiling, and then determining the excess of barium by a normal potassium chromate solution, which was added till on standing the supernatant fluid appeared slightly yellow by reflected light.

The iron was estimated by a carefully graduated permanganate solution.

Taking the molecular weight of the double salt to be 392, the following numbers were obtained:—

	Found.		Calculated.
$(\text{NH}_4)_2\text{O} =$	51.32 grms.		52.00
$\text{SO}_3 =$	160.12 "		160.00
$\text{FeO} =$	71.70 "		72.00
$\text{H}_2\text{O} =$	108.86 "	by difference	108.00
	<hr/> 392.00 "		<hr/> 392.00

The author concludes, therefore, that the formula representing the composition of this salt is  $(\text{NH}_4)_2\text{Fe}''(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .

W. S.

**Bromo-molybdous Compounds.** By A. ATTERBERG and P. CLEVE (Bull. Soc. Chim. [2], xviii, 21—23).

WHEN metallic molybdenum is heated in bromine vapour, it is chiefly converted into a yellowish-red body of the formula  $\text{Mo}_3\text{Br}_6$ , or more correctly  $(\text{Mo}_3\text{Br}_4)''\text{Br}_2$ , which may be viewed as bromo-molybdous bromide. When this is dissolved in caustic alkali, and carbon dioxide is passed through the solution, or ammonium chloride is added, the hydrate,  $\text{Mo}_3\text{Br}_4 \cdot 2\text{OH} + 8\text{H}_2\text{O}$ , is formed. It occurs in small golden-yellow crystals which lose all their water when heated in a current of carbon dioxide. By addition of acids to an alkaline solution of this hydrate, the different salts may be formed. The *chloride*,  $\text{Mo}_3\text{Br}_4 \cdot \text{Cl}_2 + 3\text{H}_2\text{O}$ ; the *fluoride*,  $\text{Mo}_3\text{Br}_4 \cdot \text{Fl}_2 + 3\text{H}_2\text{O}$ ; the *sulphate*,  $\text{Mo}_3\text{Br}_4 \cdot \text{O}_2 \cdot \text{SO}_2 + 3\text{H}_2\text{O}$ ; the *phosphate*,  $\left. \begin{matrix} \text{Mo}_3\text{Br}_4 \cdot \text{O}_2 \\ 4\text{HO} \end{matrix} \right\} 2\text{PO}$ , and the *oxalate*,  $\text{Mo}_3\text{Br}_4 \cdot \text{O}_2 \cdot \text{C}_2\text{O}_2 + 4\text{H}_2\text{O}$ , are all yellow. The *chromate*,  $\text{Mo}_3\text{Br}_4 \cdot \text{O}_2 \cdot \text{CrO}_2 + 2\text{H}_2\text{O}$ , is purple. The *molybdate*,  $\text{Mo}_3\text{Br}_4 \cdot \text{O}_2 \cdot \text{MoO}_2 + 2\text{H}_2\text{O}$  is reddish-yellow, and is obtained by adding acetic acid to a mixture of ammonium molybdate and bromomolybdous hydrate in alkaline solution. The

*nitrate* is a yellow precipitate, but it cannot be isolated, since it loses all its nitric acid by drying at 100°.

B. J. G.

## Mineralogical Chemistry.

**On a peculiar Lava Block thrown out during the Eruption of Vesuvius, April, 1872.** By G. VOM RATH (Pogg. Ann., cxlvi, 562—568).

THE author gives a detailed description of the peculiar formation exhibited by a block of lava, which seems to yield a considerable amount of information on the formation of minerals by volcanic vapours. This block shows that whilst in the peripheral zone, augite melts in the volcanic fire, and leucite is decomposed, beautiful crystals of iron glance, or specular iron, magnetic iron, augite, sodalite, and mica are formed in the inner zone. The outer portions of the block where the pores were filled with a melted mass do not contain any new minerals, but at a distance of about 12—15 mm. from the periphery, where the green augite is not completely fused, the new formation begins. The pores here are not filled with melted mass, but the walls and small crevices are lined principally with crystals of reddish-yellow augite of about  $\frac{1}{2}$ — $\frac{1}{4}$  mm. large, and with crystals of iron glance, together with leucite. In smaller quantity than the iron glance, magnetic iron occurs in beautiful octohedrons, attached to the walls of the pores, and a fourth newly-formed mineral in still smaller quantity is sodalite, which occurs in brilliant mother of pearl-like crystals. The author thinks it probable that the iron-glance is formed by a series of reactions such as the following:—Sodium chloride vapour and water vapour at the high temperature yield soda and hydrochloric acid; the latter acting on the iron forms ferric chloride which is again decomposed by the water vapour, forming specular iron; and the soda thus produced may take part in the formation of the sodalite, which contains both a sodic silicate and chloride.

A. P.

**The Dust thrown up by Vesuvius in the recent Eruption.**  
By G. GLADSTONE (Chem. News, xxvi, 97).

DURING the eruption of Vesuvius which took place last spring, Naples and the surrounding country within a radius of twenty-five miles were visited by a shower of fine black dust. It consisted of aggregations of crystallised quartz dotted over with magnetic oxide of iron. The grains were very uniform in size, and would pass through a wire gauze, the apertures of which measured the  $\frac{1}{10000}$ th part of a square inch. The iron oxide was crystalline, and possessed a high metallic lustre; it was readily soluble in hot hydrochloric acid, nothing but crystals of pure white quartz remaining.

This Vesuvian dust did not contain titanium, although in the

magnetic iron sand of New Zealand, which is doubtless of volcanic origin, titanium is present in considerable quantity.

J. W.

**Examination of Rain accompanied by Meteoric (Volcanic) Dust.** By O. SILVESTRI (*Gazzetta Chimica Italiana*, ii, 83—88).

A CYCLONE, which lasted in Southern Europe from February 24th to 27th, 1872, passed over Africa on the 28th, and appeared in the island of Sicily, on March 5th, from which date till the 11th the barometer at Palermo suffered a continuous fall of from 769·18 mm. to 758·95 mm., the wind blowing violently from the eastern points of the compass, causing a tempestuous sea, and accompanied by a dense mist. On the 9th, 10th, and 11th rain fell in Sicily, coloured reddish-yellow by a quantity of fine dust with which it was mixed. After standing a quarter of an hour, the coarser particles subsided, but it required two filtrations to remove the finer portion. One litre contained 3·3 grms. of dust. The filtered rain was without colour or smell, with a very slight brackish taste, and had no reaction on litmus; its sp. gr. = 1·00069. One litre yielded, upon boiling, 19·5 c.c. of gas, consisting, in 100 volumes, of 83·959 vols. nitrogen, 13·07 vols. oxygen, and 2·971 vols. carbon dioxide. Upon concentration, the rain assumed a yellow colour, and when it was evaporated to dryness at 100° yielded 0·66 grm. of brown residue, which blackened at a red heat and suffered a loss of  $\frac{1}{4}$  its weight of nitrogenous organic matter. One litre of filtered rain contained:—

Water.....	1000·000 grms.
Calcium dicarbonate..	0·129 „
Magnesium „ ..	0·035 „
Ferrous „ ..	traces
Calcium sulphate ....	0·041 „
Sodium „ ....	0·009 „
Potassium chloride ..	traces
Sodium „ ..	0·321 „
Organic matter.....	0·163 „
	<hr/>
	1000·698 „

There was nothing unusual about the quantity of ammonia, which = 0·00022 grm. per litre.

The dried dust consisted of shining micaceous particles, sp. gr. 2·5258. It consisted, in 100 parts, of 75·08 parts of argillaceous particles coloured by iron, 11·69 parts of calcareous particles, and 13·19 parts of nitrogenous organic matter. Examined microscopically, the dust was found to contain an abundance of such organic matter as hairs, fibres, &c., together with five classes of complete organisms, viz.:— (1.) Spherical and subspherical vesicles, diameter  $\frac{1}{80}$  mm., with very thin walls, and egg-shaped, yellowish, granular nuclei, with traces of concentric lines between the nucleus and the periphery. (2.) Discoïdal and meniscus-shaped vesicles, linear diameter  $\frac{1}{160}$  mm., having no nuclei, but with transparent, colourless walls, arranged in concentric



layers. (3.) Protei-formed vesicles, either spherical or oval, according to the pressure of surrounding particles, diameter from  $\frac{1}{100}$  to  $\frac{1}{80}$  mm., with thin, transparent, colourless, single walls. (4.) Four species of diatoms, already described by Ehrenberg in a similar instance to the present, viz., *Navicula fulva*, *Synedra Entomon*, *Pinnularia æqualis* (?), *Gallionella crenata*. (5.) Three species of infusoria of quick and ceaseless movements, viz., *Ciclidium arborum*, *Trachelius dendrophilus*, *Bursaria triquetra*, which principally revolved round the yellowish, organic, granular particles. The dust was examined immediately it was deposited, in order to obviate any objection that the organisms were developed by long exposure to air. To the suggestion that the dust was probably derived from the African Sahara, the author replies that his examination of the sand of that desert shows that it is of sp. gr. 2.5242, and is composed of—

Siliceous ferruginous particles . . . .	91.2
Calcareous particles . . . . .	8.0
Sodium chloride . . . . .	0.5
Organic matter . . . . .	0.3
	<hr/>
	100.0

No organisms are present, and therefore, in spite of the similarity of its sp. gr. to that of the meteoric dust, and notwithstanding his admission that the latter contains many objects well known in the vicinity, whence they were no doubt derived, such as the hairs of the olive leaf, &c., he concludes that the volcanic dust is not African in origin. He gives some reasons for thinking that it is derived from South America.

B. J. G.

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**Fichtelite in recent Pine Timber.** By J. W. MALLET (Chem. News, xxvi, 159).

SOME nearly colourless crystalline crusts found in clefts between the annual rings of growth of a log of long-leaved pine (*Pinus australis*) in Alabama, were found to dissolve in boiling alcohol, and to recrystallise with greater distinctness on cooling. The crystals had the composition C. 87.82, H. 11.91, corresponding to the formula  $n(C_5H_8)$ . The melting point was  $45^\circ$  C., and in chemical and physical properties the substance agreed with the fichtelite of Bromeis and Clark, a hydrocarbon hitherto found only in the fossil state.

J. B.

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## Organic Chemistry.

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**On the Normal Paraffins.** By C. SCHORLEMMER (Phil. Trans., 1872, 111).

BERTHELOT showed, 1858, that the compound  $CH_3Cl$ , obtained by the action of chlorine upon marsh-gas was identical with methyl chloride; and since that time the researches of Pelouze and Cahours, as well as

those of the author, have shown that this reaction is a general one, and that by means of it any paraffin may be converted into the corresponding alcohol. On oxidising these alcohols, acids were produced containing the same number of carbon-atoms in the molecule as the alcohols themselves, from which it would appear that they were primary ones; but a careful study of the oxidation products of octyl alcohol, which was obtained from octane contained in petroleum, gave as result that this alcohol is a mixture of methyl-hexyl carbinol with a primary octyl alcohol. This observation made it highly probable that by the action of chlorine upon the paraffins primary and secondary chlorides are formed at the same time, and further experiments with hexane fully confirmed the correctness of this supposition. The reasons why formerly the secondary compounds were overlooked are the following:—

The chlorides had to be isolated from a mixture containing, besides large quantities of unattacked hydrocarbon, also higher chlorinated products. The difference between the boiling points of the two chlorides is about  $10^{\circ}$ , but by far the greatest quantity distils between these limits at a nearly constant temperature, and this was regarded as a pure compound. To convert it into the alcohol it was heated with potassium acetate. During this operation a large quantity of the secondary chloride splits up into hydrochloric acid and an olefine, from which the acetate had to be separated by distillation, and the highest boiling portion, consisting of course chiefly of the primary compound, was used for the preparation of the alcohol, the quantity of which was so small that the acid formed by oxidising it could only be identified by analysing the silver-salt, in the preparation of which the small quantity of the ketone derived from the secondary alcohol remained in solution, and was thus overlooked. As soon as it was ascertained that by the action of chlorine upon the paraffins a mixture of two chlorides is formed, the problem next to be solved was to find the conditions under which one or the other is formed. Hexane from petroleum was therefore treated with chlorine under the following conditions:—

(1.) Dry chlorine was passed into the well cooled hydrocarbon in diffused daylight. (2.) It was acted upon in the cold by chlorine in the presence of iodine. (3.) Chlorine was passed into the vapour of the boiling hydrocarbon. (4.) Chlorine was passed into the vapour in the presence of iodine. The result was that in all four cases as first product a mixture of a primary and a secondary hexyl chloride was formed. Further, it was found that when chlorine acts in the cold, or in the presence of iodine, large quantities of higher chlorinated products are always produced, the formation of which can be almost completely avoided by passing chlorine into the vapour of the boiling hydrocarbon. In investigating other paraffins the latter method was therefore always used. The mixture of the two chlorides was next heated with glacial acetic acid and potassium acetate to  $200^{\circ}$ , the primary chloride yielding the corresponding acetate, whilst the secondary compound is partly resolved into an olefine and hydrochloric acid, and is partly converted into the acetate of the secondary radical. By treating the acetates with an alcoholic solution of potash, the alcohols are produced. Whilst neither a mixture of

the chlorides nor of the acetic ethers can be separated even approximately into its constituents, it is easy to divide the mixed alcohols into two portions, each having a nearly constant boiling point, but although apparently a complete separation has thus been effected, the bodies obtained are, as their products of oxidation show, far from being pure compounds. This might have been expected *a priori*, the difference of the boiling points of the two alcohols being only about  $10^{\circ}$ .

*Normal amyl hydride* or *pentane*,  $C_5H_{12}$ , is a mobile liquid boiling at  $37^{\circ}$ — $39^{\circ}$ , which is found in the light oils from cannel- and boghead-tar, and in large quantities in Pennsylvanian petroleum. The mixture of the two pentyl chlorides boils between  $95^{\circ}$  and  $110^{\circ}$ , the principal fraction distilling at  $100^{\circ}$ — $102^{\circ}$ . On decomposing then with potassium acetate they yield *pentene*,  $C_5H_{10}$ , boiling at  $39^{\circ}$ — $40^{\circ}$ , and acetic ethers boiling between  $135^{\circ}$ — $140^{\circ}$ . The two pentyl alcohols were separated into two portions, one boiling at  $120^{\circ}$ — $122^{\circ}$ , consists chiefly of *methyl-*

*propyl carbinol*,  $\left. \begin{matrix} CH_3 \\ C_3H_7 \end{matrix} \right\} CH.OH$ , yielding on oxidation *methyl-propyl ketone*, boiling at  $102^{\circ}$ — $105^{\circ}$ , which, on further oxidation, is resolved into acetic acid and propionic acid. The primary pentyl alcohol boils at  $134^{\circ}$ — $137^{\circ}$ , and is identical with the normal amyl alcohol of Lieben and Rossi; by oxidation it is converted into normal valerianic or *pentylic* acid, possessing all the properties described by those two chemists. From the formation of the latter acid it appears that pentane is a normal paraffin, having the constitution  $CH_3-CH_2-CH_2-CH_2-CH_3$ .

*Normal hexyl hydride* or *hexane*,  $C_6H_{14}$ , occurs in the same oils as pentane, and boils at  $69^{\circ}$ — $70^{\circ}$ . It yields a mixture of monochlorides, boiling between  $120^{\circ}$ — $130^{\circ}$ , by far the largest quantity of which distills constantly at  $125^{\circ}$ — $126^{\circ}$ , as already observed by Pelouze and Cahours. On acting on them with potassium acetate they yield *hexene*,  $C_6H_{12}$ , boiling at  $69^{\circ}$ — $70^{\circ}$ , and acetates distilling between  $158^{\circ}$ — $160^{\circ}$ , not, as Pelouze and Cahours state, at  $145^{\circ}$ . The secondary alcohol obtained

from them is *methyl-butyl carbinol*,  $\left. \begin{matrix} CH_3 \\ C_4H_9 \end{matrix} \right\} CH.OH$ , yielding on oxidation first *methyl-butyl ketone*, boiling at  $126^{\circ}$ — $128^{\circ}$ , and then acetic acid and *normal butyric* acid, which latter was identified by the characteristic properties of the calcium salt. The primary hexyl alcohol boiling at  $150^{\circ}$ — $155^{\circ}$  gave on oxidation *caproic* acid, the boiling point of which was found to be  $200^{\circ}$ — $205^{\circ}$ . Its silver-salt crystallises in small needles; the calcium salt forms shining scales or ramified needles, but the barium-salt could only be obtained as an amorphous mass.

*Hexene* from *mannite* was prepared by the action of zinc and dilute hydrochloric acid on secondary hexyl iodide obtained from mannite. The product contains besides hexane also smaller quantities of hexene and dihexyl,  $C_{12}H_{26}$ . The latter, which boils at  $202^{\circ}$ , was removed by distillation and the olefine got rid of by means of bromine. Pure hexane boils constantly at  $71.5^{\circ}$ , and has at  $17^{\circ}$  the sp. gr. 0.6630. The chlorides boiling at  $126^{\circ}$ — $130^{\circ}$  yielded a mixture of two alcohols, one boiling at  $140^{\circ}$ — $141^{\circ}$ , being *methyl-butyl carbinol*, yielding on oxidation *normal butyric* acid; and the other, which boils at  $150^{\circ}$ — $153^{\circ}$ ,



is a primary hexyl alcohol, which, by oxidation, yields a caproic acid boiling at 201°—204°, and possessing similar properties as the acid obtained from petroleum.

The only difference observed was that the acid from mannite gives a well crystallised barium-salt. The hexane from mannite and also some of its derivatives boil a few degrees higher than the corresponding compounds from petroleum. Whether this difference, as well as that of the two barium-salts, is caused by the petroleum-hydrocarbon not being a pure compound, or whether we have here a case of a fine isomerism, for which an explanation has yet to be found, is at present impossible to decide; the formation of acetic and *normal* butyric acid proves that the two hexanes are normal paraffins, having the constitution,  $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_3$ .

*Normal dipropyl*,  $\text{C}_6\text{H}_{14}$ .—To prepare this hydrocarbon allyl alcohol prepared from glycerin was converted into propyl alcohol according to Tollen's method, and from the latter propyl iodide, boiling at 100°—102°, was prepared. On adding anhydrous ether and sodium to this iodide action took place only on heating the mixture to 140°—150°. The pure hydrocarbon boils at 49°—19°, and has at 19° the sp. gr. 0.6630. It has therefore the same physical properties as the hexane from mannite, and from the mode of its formation it follows that it has also the same constitution.

*Normal heptyl hydride* or *heptane*,  $\text{C}_7\text{H}_{16}$ , occurs, together with other paraffins, in the above-mentioned oils and boils at 97.5°—98°, and not, as Pelouze and Cahours state, at 92°—94°. It yields chlorides boiling at 145°—160°, and acetates boiling between 175°—185°. The secondary heptyl alcohol,  $\left. \begin{matrix} \text{CH}_3 \\ \text{C}_5\text{H}_{11} \end{matrix} \right\} \text{CH.OH}$ , boils at 160°—162°, and yields *methyl-pentyl* ketone boiling at 150°—152°. On further oxidation it is resolved into acetic acid and *pentylic* or *normal valerianic* acid. The primary heptyl alcohol, boiling at 170°—175°, is converted by oxidation into *œnanthylic acid* boiling at 219°—222°, which was found to be identical with that prepared from castor-oil. As the secondary alcohol yields on oxidation *acetic acid* and *normal valerianic acid*, it follows that heptane has the constitution—



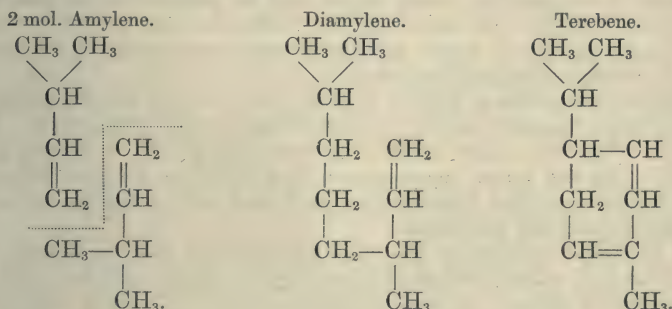
*œnanthylic acid* is consequently a normal acid, and therefore the *dihexyl*, which Brazier and Gosleth obtained by the electrolysis of this acid, is also a normal paraffin, to which the name *dodecane* may be given.

*Normal dibutyl* or *octane*,  $\text{C}_8\text{H}_{18}$ , is readily formed by the action of sodium upon normal primary butyl iodide. It boils at 123°—125°, and has at 17° the sp. gr. 0.7032. These are exactly the properties of the octane which the author obtained from methyl-hexyl carbinol and from sebacic acid, and of that obtained by Zincke from primary octyl alcohol. It appears therefore almost certain that these octanes of different origin are identical. If so, the *dioctyl*,  $\text{C}_{16}\text{H}_{34}$ , which Zincke obtained as a bye-product, is also a normal paraffin; and may be called *hexadecane*.

**On the Condensation of Amylene.** By V. v. RICHTER (Deut. Chem. Ges. Ber., v, 334).

THE author considers that the formula given by Erlenmeyer and Schneider for diamylene does not correspond with its reactions. It neither explains its power of receiving a direct addition, nor its transformation into butylene and terebene. Moreover, it assumes a symmetrical condensation, and does not account for any further condensation.

The author considers that all these requirements are fulfilled by the subjoined formula of diamylene.



In the transformation of diamylene into butylene and terebene, the closed ring of the benzene group first appears. This, being formed, we may expect the formation of a hydrocarbon,  $\text{C}_{10}\text{H}_{14}$ ; and this should be, according to the above formula of diamylene, isopropyl-methyl-benzene. This transformation of terebene has been proved by Williams, and afterwards by Oppenheim.

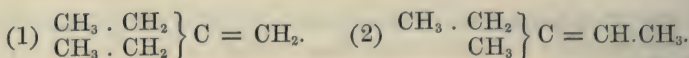
The condensation of amylene into tri- and tetra-amylene may be similarly represented, consequently one may expect to obtain isopropyl-dimethyl-naphthalene by the dehydrogenation of triamylene, and anthracene from tetramylene. The author, however, considers it probable that naphthalene and anthracene may be more readily produced from the polymeric terebenes than from the condensed amylenes. He considers those, like the amylenes, to be true atomic compounds, and not merely molecular condensations.

T. B.

**A New Hexylene.** By TSCHAIKOWSKY (Deut. Chem. Ges. Ber., v, 330).

By treating the iodide of diethyl-methyl-carbinol with potassium hydrate, a hexylene is obtained, possessing a strong odour, boiling at  $68^\circ$ — $72^\circ$ , and having a vapour-density of 42.72. When treated with hydriodic acid it yields the original iodide, and this iodide when treated with silver oxide gives again diethyl-methyl-carbinol.

The author has not determined which of the subjoined formulæ represents this hexylene.



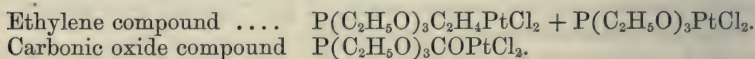
T. B.

**Study of the Phosphoplatinum Compounds.** By SCHÜTZENBERGER and FONTAINE (Bull. Soc. Chim. de Paris [2], xviii, 101—112, and 148—159). (Continued from p. 793.)

*Methylphosphoplatinous ether*,  $\text{P}(\text{CH}_3\text{O})\text{PtCl}_2$ .—Phosphoplatinous chloride acts energetically upon absolute methylic alcohol, and a liquid is obtained from which by evaporation *in vacuo*, the ether separates in the form of a crystalline mass, which may be purified by recrystallisation from benzene. It occurs in the form of orange-yellow needles, but slightly soluble in water, soluble in water containing hydrochloric acid, in alcohol, ether, and benzene.

*Ethylphosphoplatinous ether*,  $\text{P}(\text{C}_2\text{H}_5\text{O})_3\text{PtCl}_2$ .—This ether is prepared in the same manner as the corresponding methyl compound. The crystals, which are yellow anorthic prisms, melt at  $83^\circ$ , and decompose at  $180^\circ$ . At the latter temperature they evolve a mixture of ethyl chloride, ethylene, and hydrochloric acid, and leave a residue of metaphosphoric acid and platinum.

An alcoholic solution of ethylphosphoplatinous ether is decomposed by solution of silver nitrate; silver chloride is precipitated, and the corresponding nitrate formed  $\text{P}(\text{C}_2\text{H}_5\text{O})_3\text{Pt}(\text{NO}_3)_2$ . It is uncrystallisable and insoluble in water. Ethylene and carbonic oxide are rapidly absorbed by an ethereal solution of phosphoplatinous ether. Upon evaporation of the solvent the new products are obtained in the form of yellow, oily liquids, insoluble in water. They are simply products of addition, and correspond to the formulæ—

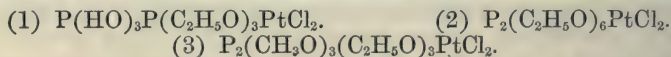


The latter compound decomposes slowly in presence of water, yielding hydrochloric acid, carbonic anhydride, and a new compound, thus—



If to a solution of phosphoplatinous ether in benzene, phosphorous chloride be added in molecular proportion, combination takes place attended with elevation of temperature, and a colourless or slightly yellow crystallisable compound is obtained. It has not been analysed, but its composition is sufficiently established by its mode of production and by the derivatives which it furnishes.

This compound,  $\text{P}(\text{C}_2\text{H}_5\text{O})_3\text{PtCl}_2$ , in contact with water yields hydrochloric acid and an acid ether (1); with absolute alcohol, it gives phosphoplatinic ether (2); with methylic alcohol, a mixed ether (3):



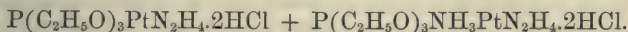
*Ammonia derivatives of phosphoplatinous ether.*—Ammonia gas is absorbed by a solution of phosphoplatinous ether in benzene, with very sensible elevation of temperature, and in a short time the liquid



becomes a semi-solid white crystalline mass. The crystals when purified and dried *in vacuo*, have the composition,  $P(C_2H_5O)_3PtCl_2 \cdot 2NH_3$ .

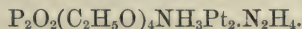
The chloroplatinate, obtained by precipitating a solution of the above salt with platinic chloride, was also examined; the percentage of platinum obtained on analysis, corresponded accurately with that calculated from the formula,  $P(C_2H_5O)_3PtCl_2 \cdot N_2H_6 \cdot PtCl_4$ .

An *alcoholic* solution of phosphoplatinous ether when saturated with ammonia, gradually loses its yellow colour, and after some hours deposits a voluminous crop of brilliant colourless crystals. These crystals yielded on analysis numbers leading to the somewhat complex formula—

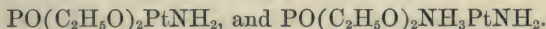


which would represent that of a double salt formed by the union of one molecule of the preceding salt, and one molecule of a salt in which  $NH_3$  *apparently* plays the same part as  $CO$ ,  $C_2H_4$ ,  $PCl_3$ , in the compounds previously described. A chloroplatinate of this latter salt was also prepared and examined.

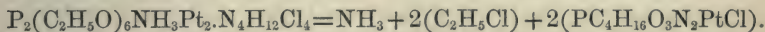
The double salt,  $P_2(C_2H_5O)_6NH_3Pt_2Cl_4 \cdot 4NH_3$ , treated with solution of caustic potash, gives, with disengagement of ethylamine, a precipitate either in the form of a colourless oil, or as a crystalline mass, according to the concentration of the potash-solution employed. The compound thus obtained is soluble in water and alcohol, but very slightly soluble in potash, which precipitates it from its aqueous solution. The crystals dried at  $100^\circ$  were found to correspond to the formula—



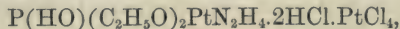
It remains to be decided whether this base is a definite product, or a mixture in equivalent proportions of the two bases—



The double hydrochloride previously mentioned when heated to  $150^\circ$ , decomposes with disengagement of  $NH_3$  and  $C_2H_5Cl$ . When the action is complete, there remains a vitreous, colourless, brittle mass; very hygroscopic and very soluble in alcohol. This residue gave the empirical formula  $PC_4H_{16}O_3N_2PtCl$ , which agrees with the equation—



The percentage of platinum yielded by the chloroplatinate of the above salt did not agree quite accurately either with the formula—



or with  $2[PO(C_2H_5O)_2NH_3Pt \cdot NH_2 \cdot HCl]PtCl_4$ . It is somewhat a matter of opinion which of these two formulæ is to be considered as correct.

The addition of chlorine-water, or excess of platinic chloride to an aqueous solution of the vitreous salt produces, after a time, a yellowish crystalline deposit, capable of being recrystallised in prismatic needles. This new salt contains neither phosphorus nor carbon, and belongs to a series of platinum compounds altogether distinct from those previously examined.

*Zinc and Phosphoplatinous Ether.*—An alcoholic solution of phosphoplatinous ether warmed with granulated zinc and hydrochloric acid, rapidly becomes of a deep brown colour, and after a short time gives, on the addition of water, a black flocculent precipitate. This precipitate washed and dried *in vacuo*, undergoes a sensible alteration; it is no longer completely soluble in alcohol, and its solubility appears to diminish, according as it is dried at a higher temperature.

Since there is no guarantee for the purity of the amorphous substance submitted to analysis, the results, as might be expected, are not very concordant. The author, therefore, wishes it to be understood, that the formula deduced therefrom, both in the present instance, and in others to be described, is put forward with a certain degree of reservation, rather as an abridged translation of the analysis than as an expression of absolute truth. The only formula which can be deduced from the analytical results is  $[P(C_2H_5O)_3Pt]_2Pt$ , or  $P_2(C_2H_5O)_6Pt_3$ .

Zinc acts also in the cold upon a neutral alcoholic solution of phosphoplatinous ether; a brown liquid is obtained, which furnishes a precipitate on the addition of water as in the previous instance. This product, however, contains zinc capable of elimination by hydrochloric acid. The platinum and zinc corresponded very fairly with the formula  $(P(C_2H_5O)_3Pt)_2Zn$ , but the percentages of carbon and hydrogen were too low. The product doubtless underwent alteration during desiccation.

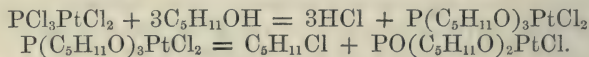
A similar solution of phosphoplatinous ether becomes brown immediately on the addition of alcoholic potash. Potassium chloride is deposited, and from the solution water precipitates brown flocculi, which when washed and dried *in vacuo*, inflame spontaneously on coming into contact with the air.

The formula,  $[PO(C_2H_5O)_2Pt]^2O$ , may probably represent its composition.

*Amylphosphoplatinous Ether.*—Phosphoplatinous chloride acts rapidly on amyl alcohol, the mixture becoming warm and disengaging hydrochloric acid. The resulting product is, however, very difficult to purify, since both the alcohol and ether are insoluble in water. It was thought better therefore to determine the composition of the ether by transforming it into an ammonia compound.

The impure ether was dissolved in alcohol, saturated with ammonia, and water added. The liquid deposited a brown, sticky mass, adhering to the sides of the vessel, but the clear supernatant liquid furnished on evaporation a crop of white pearly-looking crystals. These crystals dried *in vacuo*, gave on analysis numbers which lead to the formula,  $P(HO)(C_5H_{11}O)_2Pt.N_2H_4.HCl$ , corresponding to the ethylic monochlorhydrate previously described.

The following equations explain the reaction:—



The compound,  $PO(C_5H_{11}O)_2PtCl$ , then combines with  $2NH_3$  to form the crystalline hydrochloride.

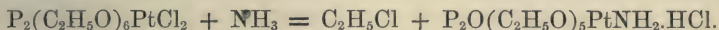
**PHOSPHOPLATINIC ETHERS.**—*Methylphosphoplatinic ether*,  $P_2(CH_3O)_6PtCl_2$ . This ether is readily prepared by dissolving the chloride,

$P_2Cl_6PtCl_2$ , in anhydrous methylic alcohol. On adding a large quantity of water to the solution the methylphosphoplatinic ether separates in the form of fine, white crystalline needles. It is insoluble in water, but soluble in alcohol, ether, and benzene. Analysis assigned to it the above-mentioned formula.

*Ethylphosphoplatinic ether*,  $P_2(C_2H_5O)_6PtCl_2$ , is prepared by the action of phosphoplatinic chloride upon absolute alcohol, in a manner similar to that which has been described for the methyl compound. Both methyl and ethylphosphoplatinic ether dissolve in caustic ammonia, and the solutions may be readily crystallised by evaporation *in vacuo*. The crystals are white, very soluble in alcohol and water, and very deliquescent. They have the following composition:—

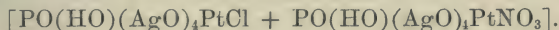
Methyl compound	....	$P_2(CH_3O)_6PtN_2H_4.2HCl$ .
Ethyl	..	$P_2O(C_2H_5O)_5Pt.NH_2.HCl$ .

In the formation of the ethyl compound, ethyl chloride is separated; thus:—

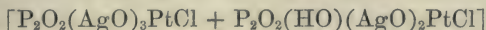


*Phosphoplatinic Acid*.—The preparation of this acid was described in a previous communication, and its composition assumed to be  $P_2(HO)_6PtCl_2$ . This formula is now confirmed by direct analysis. When phosphoplatinic acid is gently heated, it gives off hydrochloric acid and the more stable acid,  $P_2O(HO)_5PtCl$ , remains. The latter acid heated to  $180^\circ$  loses water, and is converted into a yellow non-deliquescent powder. It contains one molecule less water,  $P_2O_2(HO)_3PtCl$ .

The acid,  $P_2O(HO)_5PtCl$ , dissolved in water, gives with silver nitrate a yellowish-white precipitate. The analyses of this silver salt correspond very nearly with the formula  $P_2O(HO)(AgO)_4PtCl$ , but one-half of the chlorine is exchanged for the nitric residue  $NO_3$ . It may therefore be represented by the formula—



The dehydrated acid,  $P_2O_2(HO)_3PtCl$ , gives with silver nitrate a white precipitate, which, when dried *in vacuo*, gave on analysis numbers from which the formula—



was deduced.

The action of phosphoplatinous chloride upon glycerin, allylic alcohol, benzylic alcohol, ammonia, and the compound ammonias is reserved for a future communication.

J. W.

**On Ethylic Acetyl-oxamate.** By J. OSSIKOVSKY and G. BARBAGLIA (Bull. Soc. Chim. [2], xviii, 160—1).

THIS body is formed, together with hydrochloric acid, when acetamide is melted with ethyl chloroxalate. It forms a viscid liquid which, after long keeping, deposits crystals. It is decomposed by distillation, and



when treated with boiling water it furnishes ethyl-acetate and acid ammonium oxalate.

W. A. T.

**Observations on Amyl-nitrite.** By J. M. MAISCH (Chem. Centr., 1872, 352).

As usually prepared for pharmaceutical purposes, this body is exceedingly impure, and the author recommends the following method for obtaining a better product. Amyl alcohol, freed from ethyl alcohol by shaking with salt water and subsequent distillation, is mixed in a capacious retort with about an equal weight of nitric acid and gently warmed till boiling commences, when the fire is withdrawn and the action allowed to complete itself. As soon as the thermometer rises above  $100^{\circ}$ , the receiver is changed and the distillate obtained below that temperature is shaken with caustic lime or its carbonate, and the oily liquid remaining is again distilled and the portion coming over between  $96^{\circ}$  and  $100^{\circ}$  collected as amyl nitrite.

C. H. G.

**Action of Mercuric Cyanide and of Zinc Ethyl on Butyl Iodide.** By BUTLEROW and GERAINOU (Deut. Chem. Ges., v, 478, and Bull. Soc. Chim. [2], xviii, 124—5).

BUTLEROW found that when butyl iodide was mixed with dry mercuric cyanide, a very energetic action took place, which may be represented thus:— $C_4H_9I + Hg(CN)_2 = C_4H_9CN + HgICN$ . The product distilled with water yields an oil, which is freed from isocyanide with hydrochloric acid and again distilled. The nitrile,  $C_4H_9N$ , or  $C(CH_3)_3CN$ , passes over with other products at  $90^{\circ}$ — $120^{\circ}$ , its true boiling point being about  $103^{\circ}$ . When it is treated with alcoholic potash, then distilled from sulphuric acid, and the distillate dehydrated with phosphoric anhydride, it is converted into trimethyl-acetic acid,  $C(CH_3)_3COHO$ , which appears, on cooling, as a vitreous mass enclosing crystals. It melts at  $34^{\circ}$ — $35^{\circ}$ , boils at  $161^{\circ}$ , and is slightly soluble in water. The barium salt,  $(C_5H_9O_2)_2Ba + 5H_2O$ , is soluble in water, and crystallises in needles which lose all their water when placed over oil of vitriol. The silver salt,  $C_5H_9O_2Ag$ , is precipitated from a neutral solution in long plates, from an acid solution in needles, thus showing an inverse behaviour to that of silver valerianate.

Gerainou, by acting on tertiary butyl iodide with zinc-ethyl, has obtained a substance which he considers to be trimethyl-ethyl-formene (trimethyl-ethyl-methane), boiling at  $43^{\circ}$ — $48^{\circ}$ . Its analysis and vapour-density warrant the formula,  $C \left\{ \begin{matrix} (CH_3)_3 \\ C_2H_5 \end{matrix} \right.$ .

B. J. G.

**Allyl Alcohol Cyanide.** By TOLLENS (Deut. Chem. Ges. Ber., v, 621—622).

CYANOGEN gas when passed through allyl alcohol, combines directly with it, and the product, submitted to fractional distillation, yields a colour-

less liquid, possessing an odour similar to that of pure ethyl cyanide, which boils at about  $150^{\circ}$ , and is but slightly soluble in water. Its formula is  $C_3H_5(CN)_2OH$ , and the author believes that this dicyanide belongs to a new class of compounds in which the two cyanogen groups are directly united, besides being joined to the carbon of the allyl group.

C. E. G.

**Formation of a New Tertiary Alcohol.** By PAWLONSKY (Deut. Chem. Ges., v, 331, and Bull. Soc. Chim. [2], xviii, 124).

By the action of crotonyl chloride (obtained from sodium crotonate by heating the latter in a sealed tube at  $100^{\circ}$  with phosphoric oxychloride) upon zinc-methyl and dehydration of the product with potash, a heavy oil is obtained, boiling at  $110^{\circ}$ — $115^{\circ}$ , which may be viewed as a tertiary non-saturated alcohol, and formulated thus,  $\left. \begin{matrix} C_3H_5 \\ CH_3 \end{matrix} \right\} C.OH$ . Sodium disengages hydrogen from this substance, and bromine combines slowly with it, yielding a dense oil insoluble in water.

B. J. G.

**Hexbenzodulcitol and Tetrabenzodulcitol.** By G. BOUCHARDAT (Bull. Soc. Chim. [2], xviii, 115—118).

When one equivalent of dulcitol is heated to  $150^{\circ}$  with eight equivalents of benzoyl chloride containing benzoic acid, hydrochloric acid is evolved and the dulcitol dissolves. The temperature is then raised to  $200^{\circ}$ ; the excess of benzoyl chloride expelled by a current of carbonic anhydride; two volumes of alcohol added for one of the liquor, and the whole again heated. After some days small crystals are deposited, which, after another crystallisation from alcohol, consist of pure *hexbenzodulcitol*,  $C_6H_2(C_7H_5O_2)_6$  [or  $C_6H_8.(OC_7H_5O)_6$ ]. This body is solid and without taste or odour at the ordinary temperature. It melts at  $147^{\circ}$ ; is quite insoluble in water or ether, and only slightly soluble in alcohol. When heated to  $200^{\circ}$  and suddenly cooled, *hexbenzodulcitol* becomes amorphous, in which state it is much more soluble in alcohol, and is even soluble in ether. After a few minutes, however, crystals are deposited from these solutions, having all the properties of ordinary *hexbenzodulcitol*. The new dulcitol derivative is difficultly saponifiable. When it is treated with nitrosulphuric acid the benzoic radical is attacked and *hexnitrobenzodulcitol* is formed which, when acted on by sodium amalgam in presence of alcohol, furnishes dulcitol and sodium amidobenzoate.

When the mother-liquor obtained in the preparation of *hexbenzodulcitol*, is agitated with ether and sodium carbonate, and two volumes of alcohol are added to one of liquor, a resinous precipitate is formed, which, after drying at  $140^{\circ}$ , gives numbers on analysis, showing it to be *tetrabenzodulcitol*,  $C_6H_2(H_2O)(C_7H_5O_2)_4$  [or  $(C_6H_8)^{vi} \left\{ \begin{matrix} (OC_7H_5O)_4 \\ O'' \end{matrix} \right\}$ ]. Like *hexbenzodulcitol*, it is solid and without taste or smell at the ordinary temperature; it is insoluble in water, and only slightly soluble

in alcohol, but differs from that body in emitting, at  $150^{\circ}$ , an odour of benzoic ether, in volatilising without blackening, and in being very soluble in ether. It is saponified with difficulty. Nitrosulphuric acid apparently converts it into a nitrobenzodulcitan.

B. J. G.

**Some incomplete Experiments upon the Mutual Convertibility of Dextro- and Lævo-tartaric Acids.** By LECOQ DE BOISBAUDRAN (Bull. Soc. Chim. [2], xviii, 167—169).

THE author has kept solutions of Rochelle salt in some cases for several years, in others at a temperature of  $100^{\circ}$  for several months, with the expectation of the partial conversion of the salt into paratartrate, but has not yet examined the products.

W. A. T.

**New Modification of Pyrotartaric Acid.** By MARKOWNIKOW and TUPOLEW (Deut. Chem. Ges. Ber., v, 329).

THE authors have obtained from  $\alpha$ -brombutyric acid an *isomeric pyrotartaric acid*, which is easily decomposed by heat into butyric acid and carbonic acid. They also hope to obtain from brom-isobutyric acid a *third pyrotartaric acid*.

T. B.

**Liquid Bromotoluene.** By DMOCHOWSKY (Deut. Chem. Ges. Ber., v, 333).

THE last traces of parabromotoluene may be removed from the crude liquid bromotoluene, by treatment with chromic acid mixture as long as parabromobenzoic acid is formed.

The pure metabromtoluene which remains unacted on, when dissolved in fuming sulphuric acid, yields two sulpho acids. The barium salt of one of them,  $(C_7H_6BrSO_3)_2Ba + 2H_2O$ , is soluble in water with difficulty, and crystallises in leaflets; that of the other is easily soluble and contains no water of crystallisation. These acids when debrominated by sodium-amalgam and fused with sodium hydrate, yielded salicylic acid, and the same acid was obtained when either of the brominated acids was fused with potassium hydrate.

T. B.

**Succinyl-Benzoin.** By ADELAIDE LUKANIN (Deut. Chem. Ges. Ber., v, 331).

By the action of succinyl-chloride on benzoin the authoress has obtained *succinyl-benzoin*,  $(C_{14}H_{11}O_2)_2.C_4H_4O_2$ . It crystallises from alcohol in shining leaflets, is insoluble in water, but soluble in alcohol, ether, and carbon disulphide, melts at  $129^{\circ}$ , and is converted by alcoholic potash into benzoic acid and succinic acid.

T. B.



**On Anisic Alcohol and Methylsalicylic Alcohol.** By S. CANNIZZARO and W. KOERNER (*Gazzetta Chimica Italiana*, ii, 65—68).

*Anisic Alcohol.*—The anisic aldehyde for the preparation of this alcohol was obtained by Rossel's method (*Ann. Chem. Pharm.*, cli, 25), and subsequently purified by converting it into the acid sodium sulphite compound, and decomposing the latter with potassium carbonate. In order to obtain the alcohol, the purified anisic aldehyde is mixed with three volumes of alcohol and four or five volumes of concentrated alcoholic solution of potash and allowed to stand for some hours. When the mixture has become solid, water is added and the alcohol removed by careful distillation in a current of steam. The residue, when cold, deposits an oily layer of impure anisic alcohol, the clear, supernatant liquid consisting of an aqueous solution of potassium hydrate and anisic alcohol, from which the latter may be removed by agitation with ether. The residue left on evaporating the ethereal solution yields anisic alcohol when submitted to fractional distillation, and collecting apart the portions which come over between 250° and 260°. The first portions which come over should be tested with acid sodium sulphite, and if they give indication of the presence of anisic aldehyde, must be again submitted to the action of alcoholic potash. The alcohol, when purified by careful fractional distillation, melts at 24° to 25°; by repeated distillation, however, it becomes oxidised and reconverted into anisic aldehyde. Long contact with alcoholic potash at an elevated temperature produces a change in this alcohol similar to that which benzylic alcohol undergoes, a methylated cresol being formed whose boiling point is 174°.

*Methylsalicylic Alcohol.*—This alcohol is prepared from saligenin,  $C_6H_4.CH_2OH.OH$ , by adding to it a molecule of potassium hydrate dissolved in methylic alcohol, and subsequently digesting the mixture with methylic iodide. When the action is terminated, an aqueous solution of potash is added and the methylic alcohol removed by distillation in a current of steam; the methylsalicylic alcohol can then be extracted from the residue by agitating it with ether. The impure alcohol left on the evaporation of the ethereal solution is submitted to fractional distillation, collecting apart the portion boiling at about 240°.

The boiling point of anisic alcohol at a pressure of 760·3 mm. reduced to 0°, was 258·8° (corrected), and for the methylsalicylic alcohol 247·5° (corrected) under a pressure of 765·0 mm. Anisic alcohol melts at 25° when free from moisture, and has a density of 1·10934 at 25·85°, and 1·05067 at 99·93°. Methylsalicylic alcohol maintains its transparency when surrounded by a bath of solid carbonic anhydride and ether, but gradually thickens and becomes semifluid: in one experiment it solidified. Its density at 0° is 1·1389, and at 100° 1·0532.

C. E. G.

**The Indices of Refraction of Anisic Alcohol and Methylsalicylic Alcohol.** By P. BLASERNA (*Gazzetta Chimica Italiana*, ii, 69—75).

IN the first part of this paper the author describes the apparatus used, the methods employed, and the necessary corrections for the determination of the indices of refraction. The results are given for 28°, 29°, and 30° respectively, but the following table includes those only which were taken at 28°:—

	C.	D (half).	b.	F.
Anisic alcohol, second portion.....	1·53813	1·54308	1·55092	1·55595
Ditto, third portion.....	1·53802	1·54301	1·55080	1·55577
Methylsalicylic alcohol, second portion.	1·53951	1·54440	1·55201	1·55703
Ditto, third portion.....	1·54046	1·54534	1·55310	1·55796

C. E. G.

**On the Synthesis of Orcin, and on some Sulphur Derivatives of Toluene.** By G. VOGT and A. HENNINGER (*Ann. Chem. Phys.* [4], xxv, 129—144).

THE first portion of this paper is a more detailed account of the synthesis of orcin than that formerly published by the authors (*Compt. rend.*, lxxiv, 1107, and this volume, 621), and includes a description of cadmium chlorocresylsulphite,  $(C_7H_6ClSO_3)_2Cd + 2H_2O$ , a salt crystallising in flattened needles, which are soluble in alcohol and very soluble in water. They likewise notice the six diphenols of the cresylic series which are capable of existing theoretically, and state their reasons for believing orcin to be derived from metachlortoluene, and therefore possibly to have the formula, 1 : 3 : 5.

*Chlorobenzylsulphurous acid*,  $C_6H_4 \begin{Bmatrix} CH_2.SO_3H \\ Cl \end{Bmatrix}$ . The potassium salt of this acid mixed with potassium chloride is obtained on digesting chlorobenzyl chloride, prepared by the action of chlorine on chlortoluene with a concentrated solution of potassium sulphite. It has the formula,  $C_6H_4Cl.CH_2.SO_3K + H_2O$ , and when pure crystallises in large, flat needles. These are soluble in water and in boiling alcohol, and lose their water of crystallisation at 160°. On mixing warm concentrated solutions of potassium chlorobenzylsulphite and barium chloride, the corresponding barium salt,  $(C_6H_4Cl.CH_2.SO_3)_2Ba + H_2O$ , is deposited in needles as the solution cools. Although these salts appear to be homogeneous, they nevertheless consist of mixtures of two isomerides, for when fused with potassium hydrate, they yield salicylic and paraoxybenzoic acids, but no diphenol.

During the action of potassium sulphite on chlorobenzyl chloride, a substance is formed insoluble in water; after being washed with water and with ether and crystallised from boiling alcohol, it is obtained in colourless needles which melt at 167° and have the formula,  $(C_7H_6Cl)_2SO_2$ . As it resembles sulphobenzid,  $(C_6H_5)_2SO_2$ , in its com-

position, the authors have called it *chlorobenzylsulphide*. The mother-liquor of these crystals contains two other substances, melting at  $149^{\circ}$  and  $185^{\circ}$  respectively, but the quantity was too small for more accurate investigation.

By the action of potassium sulphite on benzyl chloride there is produced, besides potassium benzylsulphite, a body crystallising in flattened needles, which melt at  $150^{\circ}$ , and have the composition  $(C_6H_7)_2SO_2$ . This, which is *benzylsulphide*, is insoluble in water but slightly soluble in alcohol. Potassium benzylsulphite,  $C_6H_5.CH_2.SO_3K$ , fused with potassium hydrate, yields benzoic acid,  $C_6H_5.COOH$ .

C. E. G.

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**Benzoic Acid in Gas-water.** By H. REINSCH (Dingl. Polyt. J., ccv, 79).

GAS-WATER treated with gypsum yields brown-coloured, strongly-smelling ammonium sulphate. If this be dried and heated in a porcelain basin covered with a mica plate, small shining needles of benzoic acid are formed on this plate. The residue dissolved in water and filtered yields a clear solution of ammonium sulphate, while in the insoluble matter is found an aniline dye.

M. M. P. M.

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**Nitration of Alpha-toluic Acid.** By PIROGOFF (Deut. Chem. Ges. Ber., v, 332).

ACCORDING to Radziszewski, alpha-toluic acid yields by nitration both para- and ortho-nitrophenylacetic acid, which latter yields by oxidation a nitro-benzoic acid melting at  $127^{\circ}$ , and which he took for the ortho-acid. The author, however, finds that not ortho-, but meta-nitro-benzoic acid is formed. He has prepared metanitro-benzoic acid by Beilstein's method, and finds that its barium salt is more easily soluble than that of the ortho-acid. By reduction with tin and hydrochloric acid it yields anthranilic acid and finally salicylic acid.

T. B.

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**Succinylbenzamic Acid.** By MURETOW (Deut. Chem. Ges. Ber., v, 330).

By fusing succinic acid with amidobenzoic acid two acids are obtained, namely, *succinylbenzamic acid*,  $C_6H_4 \left\{ \begin{array}{l} N(C_4H_4O_2)'' \\ COOH \end{array} \right.$ , which is soluble in water and melts at  $235^{\circ}$ , and *succinylidibenzamic acid*,  $C_4H_4O_2(NH.C_6H_5O_2)_2$ , which is insoluble in water. The former is an imidogen acid, and is converted, by fixation of water, into oxysuccinylbenzamic acid,  $C_6H_4 \left\{ \begin{array}{l} NH.C_4H_4O_2.OH \\ COOH \end{array} \right.$ . The second acid is also produced by heating the first with amidobenzoic acid.

H. W.



**Camphor Acids.** By J. DE MONTGOLFIER (Bull. Soc. Chim. [2], xviii, 114).

KACHLER having asserted that Berthelot's camphic acid was only campholic acid distillable with water vapour, together with an acid resin, the author attempted to distil with water some of the camphic acid made by Berthelot (this *Journal* [2], x, 821) without succeeding in obtaining a trace of campholic acid, nor did the camphic acid, when treated with nitric acid, yield any camphoric acid, as it would have done had it contained campholic acid. The camphic acid was almost insoluble in cold and slightly soluble in boiling water.

The rotatory power of the following camphor derivatives was determined:—

Name.	Formula.	Solvent.	[ $\alpha$ ].
Camphic acid .....	$C_{10}H_{16}O_2$ .....	Alcohol.....	+ 15.8°
Camphoric anhydride ....	$C_{10}H_{14}O_3$ .....	Benzene .....	— 7.0°
„ acid .....	$C_{10}H_{16}O_4$ .....	Alcohol.....	+ 48.2°
Camphoronic acid .....	$C_9H_{12}O_5$ .....	Water.....	— 19.0°
Sulphocamphoric acid....	$C_9SO_2H_{16}O_4$ ....	.....	Inactive.

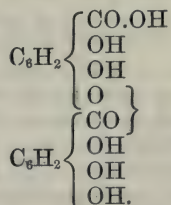
B. J. G.

**Constitution of Tannic, Ellagic, and Ruffigallic Acid.** By H. SCHIFF (Bull. Soc. Chim. [2], xviii, 23—26).

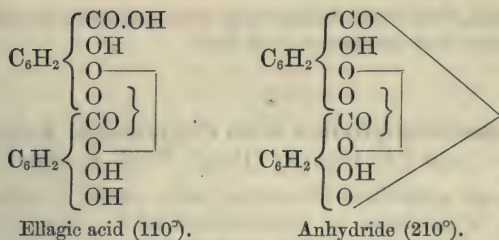
THE author in the *Bulletin*, xv, 5, and xvi, 198, gave to tannic acid the

formula, 
$$C_6H_2 \begin{cases} CO.OH \\ (OH)_2 \end{cases} O$$
, viewing it as an alcoholic anhydride of

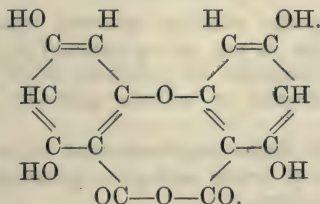
digallic acid, thus:— $C_{14}H_{12}O_{10} - H_2O = C_{14}H_{10}O_9$ . He was led to this conclusion by obtaining, on treating with acetic anhydride tannic acid made from gallic acid, what was apparently tetracetotannic acid, but which he now finds to be a mixture of a triacetic and a pentacetic derivative. Having uniformly obtained the pentacetic acid with tannic acid prepared from various sources, he now concludes that it is not an alcoholic anhydride of gallic acid, but an etherated anhydride represented by the formula—



A similar change must also be made in the formulæ of ellagic acid and anhydride, which will then be—



There seems to be no reason for changing the formula already given for rufigallic acid, which is not capable, like tannic and ellagic acid, of being transformed into gallic acid, and indeed has none of the properties of an acid. It is related to anthracene and oxyquinone in a way which will be evident on comparing with their structural formulæ that of rufigallic acid, which is probably—



B. J. G.

### The Action of Calcium Salts on Decoction of Cochineal.

By G. GUIGNET (Bull. Soc. Chim. [2], xviii, 162-4).

THE salts of carminic acid are generally violet. Pure calcium carminate however is a black precipitate which appears greenish when in thin layers. It is formed by treating carminic acid or a decoction of cochineal with calcium bicarbonate. The precipitate produced is insoluble in water and in alcohol, but dissolves in concentrated acetic acid. In contact with an excess of lime-water the black carminate becomes deep violet, the solution also assuming the same colour. The lime employed in these experiments contained no traces of iron.

W. A. T.

### Synthesis of Parabanic Acid. By PONOMAREFF (Bull. Soc. Chim. [2], xviii, 97).

By a misprint in this paper parabanic acid is stated to be obtained from urea and *parabanic acid* itself: the acid probably used was oxalic acid.

When phosphorous trichloride is poured over a mixture of this acid and urea, hydrochloric acid is given off, and what appears to be parabanic acid is produced. The silver salt of the obtained acid yields the calculated quantity of silver for the parabanate, but the free acid appears to contain one or two molecules of water more than parabanic

acid from uric acid, this water being only very imperfectly expelled by prolonged exposure at a temperature of 100°.

E. D.

**A New Decomposition-product from Commercial Aniline.** By R. BRAUN and PH. GREIFF (*Dingl. Polyt. J.*, ccv, 78).

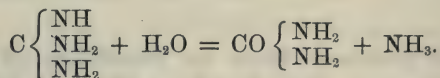
By distilling large quantities of aniline with chalk, a substance is obtained which is insoluble in hydrochloric acid. This the authors supposed to be anthracene, but they now, judging from its reactions with sulphuric acid, alkalis, &c., pronounce it to be identical with Graebe and Glaser's carbazol.

M. M. P. M.

**Researches on Guanidine.** By J. OSSIKOVSKY (*Bull. Soc. Chim.* [2], xviii, 161—2).

THE author finds that the reaction between cyanogen iodide and ammonia in sealed tubes is not, as represented by Bannow, accomplished without the formation of products other than guanidine. Ammonium iodide is formed in notable quantity, together with a volatile fatty acid.

Guanidine boiled with dilute sulphuric acid or with baryta-water, assimilates the elements of water, and gives ammonia and urea, or the products of its decomposition.



W. A. T.

**Quinine.** By C. BINZ (*N. Repert. Pharm.*, xxi, 407—410).

THE author has already pointed out that small quantities of a neutral salt of quinine arrest Brownian molecular movements (*Virch. Archiv.* xli. 151; see also concerning his researches, the abstract of Schulte's paper, *Chem. Soc. J.* [2], ix, 1202). The active movements in water of fine particles of Indian ink, pure charcoal, finely ground cinnabar, ground parts of plants, fine earth, or, best of all, of the pigment granules of the choroid, observed to go on for days together, are rapidly arrested by a neutral solution of quinine, and the particles thus caused to subside. A neutral or slightly basic solution of quinine, even in very small quantities, is nearly as powerful in causing this phenomenon of subsidence as alum, more powerful than alum neutralised with sodium carbonate, and still more so than the other officinal salts of the alkaloids. Slight alkalescence retards the process. It has but little influence over the movements of powdered gamboge.\*

Quinine also possesses in a remarkable degree the property of preventing the occurrence of certain forms of decomposition. It materially retards the conversion of cane-sugar into glucose, and checks the acid fermentation of flour. The effect of quinine salts, however, in checking



acid fermentation does not appear to be due to any peculiar property of the quinine, but to the fact that its neutral salts give off acid. Sulphate of quinine checks the process, but not to a materially greater extent than the corresponding potassium and sodium salts. On the other hand, hydrochloride of quinine, like potassium or sodium chloride, rather hastens the process.

Quinine has no effect upon the saccharifying action of saliva. But it energetically checks putrefaction, alcoholic fermentation, and the formation of lactic and butyric acids by the fermentation of sugar. The author believes that it can arrest putrefaction in the blood and other tissues.

According to von Boeck, the lessened rate of destruction of albumin in the living body caused by quinine must be ascribed to its direct influence upon (vegetative) cells. The author similarly holds that the contents of the red blood-corpuscles are undoubtedly under the influence of quinine. Quinine is also a muscle-poison.

E. D.

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**Note on Guaranine.** By JOHN WILLIAMS (Chem. News, xxvi, 97).

SOME years ago Dr. Stenhouse examined guarana, and isolated the crystallisable principle, which he termed guaranine.

The author finds that the process for preparing guaranine recommended by Stenhouse, is not only troublesome, but gives unsatisfactory results; he has therefore devised the following. Guarana reduced to a fine powder, is mixed with one-third of its weight of hydrate of lime, and moistened with water. After an hour or two, it is placed in a drying closet, and completely dried at a moderate heat. It is then exhausted with boiling benzene, filtered, and the benzene distilled off. A small quantity of light-coloured oily matter is left, which is treated with boiling water, and again digested over a water-bath, until all traces of benzene have been dissipated, then filtered through a wetted filter so as to keep back the oil; the aqueous portion evaporated to a small bulk, and set aside for twenty-four hours, yields the guaranine white and pure, and requiring no further purification.

In appearance, guaranine would seem to be identical with theine and caffeine, but the author suspects it will be found to be rather more soluble in water, and not quite so bitter in taste as the above-mentioned bodies:

J. W.

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**Distribution of Atropine in the Leaves and Roots of the Deadly Nightshade.** By J. LEFORT (Gaz. Méd. de Paris, xlvii, 433; Chem. Centr. 1872, 376).

THE alkaloid is present in the leaves before flowering somewhat more abundantly than after flowering; the leaves should therefore be collected between flowering and fructification. Cultivated and wild plants yield equal quantities of atropine at the same season. The quantity of atropine in the roots varies greatly. Young roots yield more than

roots two or three years old, because the latter contain a smaller proportion of bark.

H. W.

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**The Poisonous Principle of Ergot-of-rye.** By E. HANDELIN (N. Jahrb. Pharm., xxxvii, 157; Chem. Centr., 1872, 577).

THIS substance dissolves in water, but scarcely or not at all in alcohol. It is soluble, however, in dilute alcohol mixed with acetic acid, from which solution it is precipitated by ether, partly at least undecomposed. It is decomposed by barium hydrate, not precipitated, or only partially by potassium-bismuth iodide. By precipitation with mercuric chloride and tannic acid, it undergoes alteration, by which it loses its physiological activity. Hence it would appear that neither the substance (echoline) which Wenzell obtained from the precipitate formed by mercuric chloride, nor the ergotine obtained from the filtrate, can be regarded as the active principle of the ergot.

H. W.

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**Noctilucin.** By T. L. PHIPSON (Chemical News, xxvi, 130).

THE peculiar organic substance which causes the production of light in phosphorescent fish, the glowworm, and probably all other phosphorescent animals, appears also to be formed by a variety of circumstances at the expense of dead animal and vegetable tissue, and even by certain living plants (*Euphorbia*, *Agaricus*, &c.). The author has named it noctilucin, and his present observations relate to it only as produced in the animal world.

At the ordinary summer temperature noctilucin is a semi-fluid, almost liquid substance, containing nitrogen; it is white, contains a considerable amount of water, and has a slight odour resembling that of caprylic acid; it is only slightly soluble in water, and insoluble in alcohol and ether. Sulphuric or nitric acid dissolves and decomposes it, and potash evolves ammonia from it. When moist it absorbs oxygen and evolves carbonic acid, and, when left to itself, dries up to thin, shining, transparent films, devoid of structure, and resembling the *mucin* of the garden snail.

Recently produced, it is highly phosphorescent, and the production of light is owing to oxidation. It is secreted in phosphorescent animals by a special organ just as bile is secreted by the liver, and appears to be used in producing light nearly as fast as it is formed. Its light is nearly monochromatic, and its spectrum principally developed between the lines E and F. In an impure state noctilucin can be obtained from the surface of various fish when highly phosphorescent, also from the glowworm by pressing the luminous matter collected by the scalpel through porous filtering-paper. It is secreted in a pure form by the luminous centipede (*Scolopendra electrica*).

J. B.

**Colouring-matter found in the Sarcophagus of St. Ambrose at Milan.** (*Gazetta Chimica Italiana*, ii, 78—81).

THIS colouring-matter which was found to have been deposited as a sediment in the tomb of St. Ambrose, after the water it contained had been removed, was of a reddish-violet colour, and had mingled with it both the earthy substances left by the water and the products of decomposition of the tissue of the vestments. As it might reasonably be supposed that this sediment contained the colouring-matter of the vestments in which the body of St. Ambrose was clothed when deposited in the sarcophagus in the ninth century, it seemed of interest to ascertain, if possible, of what the colouring-matter consisted. After removing the earthy substances, &c., by treatment with warm dilute hydrochloric acid and very dilute potash, the residue, at first suspected to be the Tyrian purple of the ancients (that of the murex), was examined and found to consist of a mixture of two colouring substances. On treating it with weak alcoholic potash, a red substance was dissolved leaving a blue residue which was proved to be indigo: the alcoholic solution, neutralised with hydrochloric acid and diluted with water, deposited a reddish-coloured resin, which, from its properties, appeared to be identical with lac.

C. E. G.

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**Preparation of Albumin.** (*Dingl. Polyt. Jr.*, ccv, 78).

SCHWALBE states that if a drop of mustard-oil be added to 20 grams of milk, the latter does not curdle, but its casein is, after some time, changed into albumin.

Albumin may thus be cheaply prepared.

M. M. P. M.

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**Physiological Chemistry.****The Variations in the Proportions of Water, Fat, and Nitrogen in Flesh.** By P. PETERSEN (*Zeitschr. f. Biologie*, vii, 166; *Chem. Centr.*, 1872, 280—287).

THIS investigation was undertaken in order to test the truth of Voit's much-controverted assumption that the percentage of nitrogen in flesh is an almost invariable quantity, viz., 3.4 per cent. The author finds that the proportion of nitrogen varies with the quantities of water, fat, and connective tissue respectively contained in the flesh. The muscle of the horse, ox, sheep, and pig was operated on, and the specimens were invariably taken either from the ham or from the fore leg immediately after the slaughter of the animal, and every precaution was taken to avoid errors.

The percentage of water had a range of 7.36 p. c., viz., from 79.29 p. c. in the calf to 71.93 p. c. in the pig. The mean was 76.2 p. c., a result in close accordance with Voit's determinations (75.9—75.67 p. c.).



Estimated by Will and Varrentrapp's method, the nitrogen ranged from 11.88 to 15.07 p. c. of the dried flesh; and from 3.03 to 3.64 of the undried flesh. The means were 13.79 and 3.27 p. c. of the dried and undried flesh respectively. Voit found 3.4 p. c. nitrogen in fresh muscle. The following means were obtained for various kinds of fresh meat:—Beef, 3.29; pork, 3.25; mutton, 3.15; veal, 3.18; horse-flesh, 3.48.

Nowak's statement (vide this *Journal*, x, 512) that Will and Varrentrapp's method of determining nitrogen gives too low results when employed for the analysis of muscle is confirmed; but it is shown that the error introduced by the former method is insignificant when the analyses have reference to undried muscle.

An excess of water in muscle was found to be associated with an excess of nitrogen and a deficit of ethereal extractives (fat). In all cases the muscle in these experiments was freed from visible fat and tendon previous to being weighed for analysis. Excluding pork, which is difficult to free from fat by mechanical means, the ethereal extractive ranged from 0.76 to 3.4 p. c. of the undried flesh: mean 1.76. Two per cent. is adopted as the mean of fat in lean flesh, pork included.

Correction being made for the small quantity of nitrogen in the ethereal extractives (for which we must refer to the original paper), the following are adopted as the means of nitrogen in fresh lean flesh:—Beef, 3.38; pork, 3.41; mutton, 3.24; veal, 3.20; horse-flesh, 3.53 per cent.

T. S.

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**Comparative Examination of the Muscular Substance of the Heart in a case of rapid Death with and without Fever.** By E. SALKOWSKI (Pflüger's *Archiv. f. Phys.*, v, 213).

ON examining the heart of a patient who died of apoplexy, without previous illness or disease of the heart, and that of one who died of pneumonia with high fever, it was found that the latter contained very little more potash than the former. The author has also been unable to detect any increase of potash in the serum of feverish patients. Potash salts are evidently excreted from the organism as soon as they are set free by transformation of the tissues.

T. L. B.

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**On a Fermentative Action of the Blood.** By E. TIEGEL (Pflüger's *Archiv. f. Physiol.*, vi, 249).

THE author attempted in vain to separate the hepatic diastatic ferment by treating dried and pulverised livers with glycerin or with solutions of various salts. When dog's liver was rubbed up with solid sodium chloride and washed with saturated solution of salt, the latter portions of the filtrate were free from sugar, but showed a decided diastatic power when digested with starch-mucilage.

All attempts to separate the ferment from this solution failed, as all precipitants seemed to destroy its activity. The hepatic appears to differ from the pancreatic ferment in being insoluble in glycerin.

When blood-corpuscles are in process of destruction, the blood has a decided diastatic power, and converts both glycogen and starch into sugar, but it has no such action either when the corpuscles are perfectly intact or when they are completely destroyed.

This property is shown by mixing blood with glycogen solution and adding sodium glycocholate or ether to destroy the blood-corpuscles. It also acts as a ferment during its coagulation. Solid glycogen is not changed by the blood, its conversion occurring only when in solution. The author supposes that the conversion of glycogen into sugar in the liver is due to a destruction of blood-corpuscles taking place in its capillaries, the glycogen probably existing partly in a dissolved state, and being transformed in the capillaries rather than in the hepatic cells. This view is confirmed by an experiment which he made at Kühne's suggestion, in which he found that the glycogen taken up by water passed through the portal vein of a rabbit's liver became converted into sugar if blood were present in the liquid, but did not do so if the blood were completely removed. He distinguishes three kinds of diabetes. 1st. When the glycogen is not increased, but the destruction of blood-corpuscles is more rapid. To this class belong Harley's method of injecting chloroform, ether, alcohol, or ammonia into the portal vein, and the author's experiments, in which he occasionally succeeded in producing diabetes by injecting very slowly  $\frac{1}{4}$ — $\frac{1}{2}$  c.c. of ether into the vein of the ear and repeating it at intervals. 2nd. When the glycogen is not increased nor the destruction of corpuscles more rapid, but more glycogen is dissolved in the liver. An example of this is the production of diabetes by injection of 1 per cent. salt-solution into the arteries. 3rd. Artificial increase in the amount of glycogen by injection into the vessels.

T. L. B.

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**Physiology of Human Bile.** By v. WITTICH (Pflüger's Archiv. f. Physiologie, vi, 181—184).

VON WITTICH criticises a statement made by Ranke in his *Physiologie*, viz.: "The bile of the pig, as Nasse has shown, possesses the power of converting starch into sugar. Neither the bile of other animals nor of man possesses this property." He points out that he and Jacobson had already shown that this was not the case. The difficulty in regard to human bile is the possibility of obtaining it quite fresh. Von Wittich has been fortunate enough to obtain bile, perfectly fresh, and in sufficient quantity for experimentation, from a patient labouring under a biliary fistula opening externally.

Careful calculation of the amount poured out gave an average of 22.2 c.c. per hour, and 532.8 c.c. in the twenty-four hours.

Boiled starch mixed with from twenty to thirty drops of bile, and left for an hour at the ordinary temperature, gave a distinct sugar reaction with copper sulphate. The bile, mixed with absolute alcohol as long as it exhibited turbidity, left on filtration a residue which, on being treated with glycerin, yielded an extract which, after twenty-four hours, possessed an energetic diastatic action. Still more active was the alcoholic precipitate of the extract dissolved in water. Human bile therefore appears undoubtedly to contain an active diastatic ferment.

D. F.

**Occurrence of Hypoxanthine in Normal Bone-marrow.** By PAUL HEYMANN (Pflüger's Archiv. für Physiologie, vi, 184—189).

SALKOWSKI had found hypoxanthine in the marrow of leukamic patients, but had left it undecided whether it occurred also normally there or not. Heymann, under the direction of Kühne, investigates this point. For particulars of method, reference must be had to the original.

In the watery extract of the marrow of the bones both of man and of the calf, after removal of other substances, silver nitrate causes a precipitate which has the characters of the silver-compound of hypoxanthine. This, on separation of the silver, leaves a substance which, in its chemical and microscopical characters, agrees with hypoxanthine.

Cholesterin is likewise found in the marrow, but gelatin, which is stated by some to be a constituent, is really a product of ossein formed by the process of extraction, and does not exist in the marrow as such.

D. F.

**Appearance of Sweet and Skim Milk under the Microscope.** By BOUSSINGAULT (Dingl. Polyt. J., ccv, 65—68).

BUTTER-MILK under the microscope appears very different from milk from which no butter has been made; it contains, however, a certain amount of the characteristic butter-globules.

The author's experiments show that the fourth part of the entire amount of butter remains in the butter-milk. In sweet milk the butter globules are numerous and crowded together; in butter-milk they are fewer, and widely separated from one another.

By the gathering together of these butter-globules, cream is formed on the surface of milk—milk which contained 3.62 per cent. butter, after standing 24 hours, still showed 1.4 per cent.—so that all the butter globules do not collect in the cream; a good cream contains 37—40 per cent. butter.

Skim milk contains less butter than butter-milk; the latter is therefore often adulterated with the former, but this admixture of skim milk may be detected by the microscope.

M. M. P. M.

**Influence of Food containing little or no Phosphoric Acid on the Composition of Bones.** By H. WEISKE (Zeitschrift f. Biologie, vii, 133—179; Chem. Centr. 1872, 427).

THE author concludes from his experiments that the removal of lime or phosphoric acid from the food of an adult goat has injurious results, and finally causes death, but has no influence on the composition of bones, and can hardly render them brittle.

T. L. B.



**Digestion of Mineral Substances by Animals (Preliminary Note).** By R. V. TUSON (Chem. News, xxv, 138).

CALOMEL is not dissolved by the single action of either pepsin and water, or of a 2 per cent. solution of hydrochloric acid, at 38° C., but it is dissolved by a mixture of the two. Its digestion, by artificial gastric juice at least, is thus shown to take place under the same conditions as that of albuminoids.

B. J. G.

*Physiological Action of Opium Alkaloids.* By RABUTEAU (Compt. rend., lxxiv, 1109; also by BOUCHAT, *ibid.*, 1289).

**Chemistry of Vegetable Physiology and Agriculture.**

**Influence of the Spectrum Colours on the Decomposition of Carbon Dioxide by Plants.** By W. PFEFFER (Versuchs-Stationen Organ., xv, 256—367).

LEAVES of *Elodea canadensis* were exposed in a vessel of water to the different coloured rays of a spectrum 230 mm. in length, produced by means of a heliostat, prism, and leuses. The amount of decomposition of carbon dioxide was measured by counting the number of bubbles of gas disengaged in a fixed time, as described in a previous paper (*Bot. Inst. Würzburg*, 1871). This method was preferred to measuring the decomposed gas, as requiring less time of exposure, and because the same leaf can be used for different colours. The results by this method are very concordant among themselves, but as the stream of bubbles becomes slower, the numbers become rather too high, and a tendency in the same direction is caused by the light not being perfectly homogeneous. The maximum decomposition takes places at the point of the highest intensity of the light rays near D towards E, and if the leaves be placed here and then moved even a little either to the right or left, a slight decrease in the number of bubbles is observed. If the amount of decomposition for yellow be taken at 100, then red = 25.4, orange 65, green 37.2, blue 22.1, indigo 13.5, violet 7.1. The value of the rays corresponding to the absorption-band I of chlorophyll solution is 29.1. The exact limits assigned to the colours and other particulars will be given in the *Botanische Zeitung*.

On comparing the curve produced with the above numbers as ordinates, with Kerordt's curve of the intensity of light, it is found to agree closely, and, taking into account the known errors of the method, the real assimilation-curve would be still more in accordance with the light curve.

These results contradict the theory of Lommel (*Pogg. Ann.*, cxliii, 568), that those rays between B and C, which are most readily absorbed by chlorophyll solution, and have a high mechanical intensity, are those which are most powerful in promoting assimilation, and confirm the conclusion arrived at before by Draper and the author, that the physiological intensity of light corresponds with its intensity to our eyes.

E. K.

**Influence of Sulphurous Oxide on Plants.** By JULIUS SCHROEDER (Versuchs-Stationen Organ., xv, 321—355).

It is found that of the trees living in an atmosphere containing sulphurous oxide, as in the neighbourhood of smelting works, the coniferæ suffer more injury than ordinary foliated trees. Experiments were made to find the causes of the injury, and their relation in these two kinds of plants. Pine and alder were chosen as possessing differently constituted leaves, and the former being more sensitive in nature to the action of sulphurous oxide than the latter.

Twigs of each plant were placed under a glass shade, with a quantity of sulphurous oxide equal to  $\frac{1}{1000}$  volume of the air, the gas being renewed once after the smell had disappeared; after 36 hours the sulphuric oxide in the ash was estimated, and it was found by comparison with the ash of the normal plant, that 1,000 square centimeters of the pine-leaves had absorbed 1.6 c.c., and the same surface of alder leaves 7.9 c.c. of sulphurous oxide.

Experiments with sycamore, birch, oak, and pear leaves showed that the number of the stomata of the leaf bears no proportion to the amount of gas taken up; for the sycamore with the largest number of stomata took up the smallest quantity, and the pear leaves with the smallest number of stomata, the largest quantity of sulphurous oxide.

Leaves of *Petasites vulgaris* absorbed essentially the same quantity of gas by either their upper or under surfaces, but in the latter case the injurious action on the colour of the leaves was observed much sooner; but the leaves when dried had all the same brown colour. Sycamore leaves, whose upper surfaces were exposed for one hour to sulphurous oxide, lost in eleven hours 70 per cent. of their water; when the under surface was acted on, 74 per cent.; and when not acted on at all, 66 per cent. Therefore the quicker drying of the leaves is one of the results of the action of sulphurous oxide; and since the leaf is more affected when its under side is exposed, it seems that the stomata are influenced, and through them the transpiration of water.

*Transpiration under the influence of Sulphurous Oxide.*—Two similar twigs of a sycamore were arranged, so that the water transpired could be weighed; one was then kept in the ordinary air, and the other placed in air containing  $\frac{1}{1000}$  volume of sulphurous oxide, which was once renewed in the course of six hours, after which time the twig was removed from the action of the gas. The twigs were kept for 27 hours under the same conditions as to light and temperature, being four hours in direct sunlight, and at intervals during the whole time the amount of water evaporated from the leaves was estimated. The ratio between the total amount of water transpired, for equal surfaces, by the leaves not acted on with sulphurous oxide and those under its influence was 3.8 : 1.

In similar experiments with chestnut-shoots lasting 46 hours, of which time they were four hours in direct sunlight, the one being kept the first two hours in air containing  $\frac{1}{1000}$  vol. of sulphurous oxide, the ratio of the transpired water was 3.6 : 1. With fir twigs under the same conditions, the water was 2 : 1. With oak-leaves, but in diffused light, only 1.73 : 1, and with red beech in diffused light, 1.29 : 1.

In the leaves submitted to the action of sulphurous oxide, those parts



near the larger veins become of a clear pale-yellow colour, while the parts farther removed become pale and faded, thus making the arrangement of the veins appear very distinctly. When they were placed in direct sunlight, drops of moisture resembling honey-dew appeared on the clear green veins. It is obvious that by the action of the sulphurous oxide the normal relation between the absorption, transmission, and transpiration of the water is disturbed, and that the water taken up goes to the veins and is not transmitted further. Experiments also proved that a decrease in the amount of the gas caused less disturbance in the amount of transpired water, though no simple proportion between the amount of the gas and of decrease was indicated. It was also seen that the amount of sulphurous oxide taken up by the leaves in the dark and with a lower temperature and moister air, is smaller and its injurious effects much less marked than in the light and with higher temperature and moister air; therefore the same amount of sulphurous oxide in the air is much less injurious to plants during the night than in the day time.

Trials with beech and fir twigs showed that whilst the amount of transpiration of the former was distinctly lessened in air containing  $\frac{1}{10,000}$  part of sulphurous oxide, that of the latter was hardly affected, nor even in air containing  $\frac{1}{5000}$  sulphurous oxide.

The author concludes that the amount of sulphurous oxide absorbed by pine-leaves is smaller than that absorbed by trees with ordinary foliage for equal surfaces, and as its effect on transpiration is less in the case of the pine, the cause of the greater injury to pine trees in nature must be due to the longer duration of the leaves, whereby the injury accumulates in them, whilst in trees with annual leaves the hurt to one year's foliage would have only an indirect influence on that of the following year.

E. K.

### **Injurious influence on Vegetation of the Fumes from Smelting Works and Coal Fires.** By A. STÖCKHARDT (Der Chemische Ackersmann, 1872, 24—47, and 111—121).

THE author describes in detail the destructive effects of the Freiberg lead-smelting works. In the vicinity all vegetation was destroyed, and a pine forest at the distance of four miles was considerably injured. Cattle feeding on the fodder of the district suffered special sicknesses. Analysis showed that the affected plants contained traces of arsenic and lead, and an abnormal quantity of sulphuric acid. Experiments were made as to the cause of injury.

Young fir trees in an open garden were covered by a suitable case, and subjected to a known fumigation for two hours; the case was then opened and free access of air permitted. Eighty-six such fumigations with the vapour of arsenious oxide produced no effect on the tree. Vegetation is not destroyed in the neighbourhood of arsenic factories. When arsenic is applied in solution to the roots of plants it is far more prejudicial. Finely-powdered lead carbonate was dusted from time to time on a young fir during one year; there was no growth during this year, but in the next season the tree was healthy and vigorous. Sulphurous oxide proved most destructive. Five fumigations with air



impregnated with  $\frac{1}{18,000}$  vol. of this gas caused all the leaves to fall, and killed the upper part of the tree. Excessively dilute atmospheres produced equal injury when applied for longer times. Fir trees placed in a room and treated with 335 fumigations of  $\frac{1}{1,000,000}$ , extending over three months, were quite killed; the trees kept moist were first affected. Soot appeared to be quite innocuous. Benzene was burnt under the case surrounding a young fir till the tree became quite black; it nevertheless produced its annual shoots, and remained quite healthy. The author concludes that sulphurous oxide is the poisonous ingredient of the smoke from smelting-works. The injury from this cause is less than formerly, as the sulphurous oxide from roasting ore is utilised for the manufacture of oil of vitriol.

Handtke and Freytag have experimented on field crops. In an atmosphere containing  $\frac{1}{55,000}$  sulphurous oxide, the destruction of the chlorophyll-grains in wheat, oats, and peas, appears in a few hours; but, curiously, in a dilution of  $\frac{1}{74,000}$ , no injury takes place. Cabbages, and all plants having large strong leaves, are less affected. The fir tribe are far more susceptible to sulphurous oxide than deciduous trees; of the latter, white-thorn, beech, birch, and fruit trees are most affected; poplar, alder, and mountain-ash least.

Wood smoke has no injurious effect on vegetation, but the smoke of coal and of some kinds of turf is very prejudicial; the injury is due to the sulphurous oxide produced on combustion. The leaves and twigs of trees poisoned by coal-smoke contain an abnormal amount of sulphuric acid.

R. W.

### Distribution of Diastase in Malt. By ANTON URBAN (Chem. Centr., 1872, 332).

THE author sifted malt through sieves containing from 6·2 to 34·0 meshes to the centimeter, and submitted the various portions left on the sieves and that which passed through the finest, to the infusion process, with the results embodied in the following table:—

Meshes to the centimeter.	Grams of residue left on the sieve.	Grams of extract obtained.	Grams of sugar obtained.	Extract per 1 part of sugar.
6·2	31·5	7·620	3·626	2·10
8·0	12·4	5·870	2·172	2·70
11·9	19·6	12·019	4·851	2·45
15·4	8·3	5·415	2·532	2·12
34·0	11·0	7·494	2·893	1·92
Passed through the sieve.	18·0	14·076	6·755	2·08
Total .....	100·8	52·494	23·829	—
Normal salt .....	100	60·68	28·66	2·12

From the circumstances that a higher yield of extract per 1 part of sugar was formed by the residues left on the second and third sieves than by the normal malt, and that the total extract and sugar obtained

from the various residues jointly was less than that from the normal malt, the author concludes that the diastase is contained in excess in some one layer; that when the different portions are separated by sifting, this excess is inactive, but that when they are employed together this excess compensates for the deficiency in the poorer layers, thus increasing the total yield of extract and sugar.

The excess (100·8) of total residues left on the sieves over the quantity taken (100·0) is caused by absorption of moisture from the air during the sifting.

C. R. A. W.

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**Amount of Sugar in Hops.** By V. GRIESSMAYER (Chem. Centr., 1872, 361).

THE author has determined the amount of grape-sugar in hops from Schwetzingen to be 3·7 per cent.

M. M. P. M.

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**Proportion of Starch in Various Sorts of Potatoes.** By RAAB (Chem. Centr., 1872, 424).

IN sixty-one varieties, English, French, and German, the proportion of dry substance was found to vary from 16 to 34, and that of starch from 9 to 26 per cent.

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**On the Presence in Certain Fibres of a Substance Susceptible of some striking Colorific Changes when Chemically treated.** By W. SKEY (Chem. News, xxvi, 125).

CERTAIN fibres, among which is *Phormium tenax* (New Zealand flax), contain a substance quite distinct from the fibre, which is insoluble in water, alcohol, ether, chloroform, and dilute hydrochloric acid. This substance cannot be removed without injuring the fibre, and is probably in chemical combination with it. From its deportment with certain reagents, those fibres which contain it can easily be distinguished from those which do not. Chlorine, hypochlorous acid, and chromic acid turn the fibres which contain it a pale yellow, changed by alkalis or alkaline carbonates to a beautiful rose-red; acids restore the yellow colour. Alkalis turn the fibres yellow; nitric acid, a red-brown; dilute sulphuric acid, quite yellow; and if treated for a long period with chlorine, hot chromic, or nitric acids the fibres are completely whitened, but deteriorated in strength; ammonia or sulphuric acid has then no colouring effect upon them.

J. B.

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**Sea-weed as a Manure.** By W. FINNO (Ann. der Landwirth. Wochenblatt, 1872, 423 and 429).

ORDINARY wrack, consisting principally of *Fucus vesiculosus*, contains water, 70·57; nitrogenous substances, 2·01; cellulose, 22·05; and ash, 18·25 per cent. The protein substance contains 21·56 per cent. of

nitrogen and 2.51 of sulphur: therefore the wrack contains .32 per cent. of nitrogen; in one specimen .58 was found. The dry ash of *Fucus vesiculosus* was found to contain  $K_2O$  7.93,  $P_2O_5$  2.01, and  $SO_3$  29.74 per cent. Other specimens of the ash of sea-weed were found to contain from 8.98 to 20.75 per cent.  $K_2O$ , 2.14 to 5.64  $P_2O_5$ , and 24.6 to 28.8  $SO_3$ .

Thus wrack compares favourably with farmyard manure in its chemical composition, with the exception of being poorer in phosphoric acid, and it decomposes with equal facility. The quantity of phosphoric acid and also of nitrogen are often considerably increased by the presence of sea animals. Its value as a general manure would be much increased by the addition of bone meal or other phosphatic manure. The large quantity of sulphur compounds in sea-weed render it suitable for the leguminosæ; in some cases where potash and sulphuric acid are required the ash might be used with advantage.

Some sea-weeds, as *Zostera marina*, are not valuable as a manure, owing to the difficulty with which they decompose.

E. K.

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**Manuring with Straw.** By C. E. BERGSTRAND (Ann. d. Landwirtschaft, Wochenblatt, 1872, 231).

SUPERFLUOUS straw is easily converted into manure by rotting it in heaps with a little rape-cake or other ferment. Manure so prepared contained—

Water.	Organic matter.	Ash.	Nitrogen.	Phosphoric acid.	Potash.
74.36	15.63	10.01	.23	.10	.17

Compared with good dung it is deficient in nitrogen, phosphates, and potash. If to 12,000 lbs. of such manure 100 lbs. superphosphate, and 100 lbs. ammonium sulphate be added, it will equal the best dung, same in potash.

R. W.

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**Malden Island Guano.** By J. FITTBOGEN (Ann. d. Landwirtschaft, Wochenblatt, 1872, 310).

THIS recently-introduced guano is in the form of a coarse powder of a bright brown colour. Analysis gave the following percentage results:—

$Fe_2O_3$ .	$K_2O$ .	$Na_2O$ .	$MgO$ .	$CaO$ .	$P_2O_5$ .	$SO_3$ .	$CO_2$ .	Cl.	Sand.	Organic matter.	Water.	N.
.26	.28	1.71	1.86	43.51	37.58	.22	2.61	.82	.01	6.64	4.70	.29

This guano is similar to that from Baker Island; it is excellently adapted for the manufacture of superphosphate.

R. W.

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*Nitrogen as Plant-food.* By A. STÖCKHARDT (Der Chemische Ackersmann, 1871, 109, 129; and 1872, 81). An essay on the main points of the subject.



## Analytical Chemistry.

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### **New Method of Spectral Analysis.** By TIMIRAESEF (Deut. Chem. Ges. Ber., v, 328).

THE telescope of an ordinary spectroscope is replaced by a microscope, which is so placed that the spectrum may be reflected by the plane mirror. Under the stage is placed an objective which can be so adjusted as to make the spectrum-image fall in the same plane as the object to be investigated. One half of the slit being now screened by the solution of which it is desired to produce the absorption-spectrum, the observer perceives the continuous spectrum and the absorption spectrum side by side. The latter can now be conveniently compared with the lines produced in the former by the solid object on the stage. The absorption spectrum of single grains of chlorophyll was thus found to be identical with that of its solution; and the displacement of the skin-absorption lines, which has been observed when whole leaves are submitted to examination, was found to arise from the superposition of spectra.

T. B.

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### **Adjustment of Volumetric Test-Solutions.** By F. MAXWELL (Chem. News, xxvi, 159).

THE following method is suggested as being less tedious than that usually employed. Suppose a deci-normal solution of oxalic acid to be taken as a basis, and it is desired to make a deci-normal solution of soda exactly to correspond. A jar, say of 45 or 50 litres capacity, of soda-solution is made up by guess, and on titration 88 c.c. are found to neutralise 100 c.c. of the acid: 500 c.c. of water are added, and it is now found that 93 c.c. correspond to 100 c.c. of acid. The liquid, therefore originally required to be lowered by 12 per cent., and the addition of 500 c.c., reduced it 5 per cent. A simple calculation shows that 700 c.c. more water will bring the solution to the desired strength. If the alkaline solution be made up too weak originally, a strong solution of soda must be substituted for the water, and the adjustment proceeded with as before.

J. B.

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### **Retardation of the Precipitation of Barium Sulphate in presence of Nitric Acid and Ammonium Nitrate.** By C. GILKOWSKY (Deut. Chem. Ges. Ber., v, 3301).

AN increase in the quantity of nitric acid present is found to produce a greater amount of retardation than an increase in the ammonium salt.

H. W.

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**Estimation of Sulphur in Coal, and in Organic Compounds.**

By W. G. MIXTER (Am. J. of Sci. [3], iv, 90—96).

It is impossible to furnish a complete abstract of this paper without reproducing the drawing of the apparatus by which the process is illustrated.

The organic substance containing the sulphur to be estimated, is burned in a stream of pure oxygen, the apparatus being arranged in such a manner that while a continuous stream of gas is maintained, none of the products of combustion are permitted to escape. The sulphur oxides are condensed principally in the moisture produced during the combustion, and the complete oxidation of the sulphurous acid is effected by the introduction of a little bromine-vapour while the operation is proceeding. The sulphuric acid produced is subsequently collected, and estimated as barium sulphate in the usual way.

Owing to the large quantity of oxygen required (from 4 to 10 litres), a considerable amount of water is necessary to rinse the containing vessel thoroughly; the wash-waters therefore measure at least 500 c.c., and require concentration before the estimation is proceeded with. If the substance is not wholly volatile, a portion of the sulphur may remain behind in the form of sulphate. This must be estimated separately, and the percentage added to that obtained in the preceding operation.

The author is satisfied that the results obtained by this method are perfectly trustworthy, and appends test-analyses showing the accuracy which may be obtained. The following are some of the examples:—

	Weight taken.	Per cent. found.	Per cent. calculated.
Sulphur .....	0.207	99.76	100.0
Ditto .....	0.4951	99.93	"
Carbon disulphide....	0.7725	84.12	84.21
Ditto .....	0.4598	84.16	"
Bituminous coal.....	0.664	2.97	—

J. W.

**Examination of Superphosphate.** (Ann. der Landwirthschaft, Wochenblatt, 1872, 345—346).

At a meeting of several chemists at Magdeburg, with the view of obtaining uniform results in the analysis of superphosphates, it was decided to use the following processes for the estimation of soluble phosphate: 20 grams of the superphosphate are crushed in a mortar with water (not rubbed fine) and placed in a litre flask nearly filled with water; if the superphosphate contains little ferric oxide and alumina, the flask is shaken frequently during two hours, filled to a litre and filtered; in the presence of more ferric oxide and alumina, the solution, after careful shaking, is filtered at once.

For the estimation of the phosphoric acid, if less than 1 per cent. of phosphates of iron and alumina is precipitated by the addition of sodium acetate, the solution is titrated with uranium nitrate; if

more than this amount of phosphates is precipitated by sodium acetate, the molybdate process of Fresenius is employed. The uranium nitrate should be standardised with a solution of monocalcic phosphate, as, if sodium phosphate is employed, the results with the superphosphate solutions come out about .1 per cent. of  $P_2O_5$  too low, owing to calcic phosphate being carried down with the uranium phosphate even when the solution is not heated until nearly the whole of the necessary quantity of uranium nitrate is added. Magnesium chloride should be used for the magnesia mixture, as with magnesium sulphate, the results are a little too high, the precipitate retaining some of the salt.

It is found that the various modifications suggested for the extraction of soluble phosphate produce little or no effect on the quantity dissolved, save in superphosphates rich in ferric oxide, in which case longer contact with water causes a diminution in the quantity of soluble phosphoric acid.

E. K.

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**Testing of Commercial Iodine.** By J. A. WANKLYN (Dingl. Polyt. J., cv, 57—60, from "The Mechanics' Magazine").

THE iodine weighed in a stoppered tube is quickly transferred to a large beaker containing 40 c.c. of freshly prepared concentrated sulphurous acid solution. When the iodine is dissolved (the solution being filtered if necessary), half a litre of boiling water is added, then ammonia in excess, and silver nitrate, the precipitate is treated in the usual manner. To the filtrate from this precipitate nitric acid is added, and the silver chloride estimated. The ash is also to be estimated by igniting 5 grams of the sample.

The water may be approximately estimated by bringing 1 gram of the sample into a narrow glass tube, graduated into tenths of a cubic centimeter; 20 c.c. of carbon disulphide is added, which dissolves the iodine; the solution now occupies 200 divisions of the tube. The tube being well corked, is set aside for 2—3 hours, when the water separates out, floating on the surface of the carbon disulphide.

Suppose this layer occupies  $\frac{1}{10}$  c.c.; its weight will be .1 gram, and the sample will contain 10 per cent. water.

M. M. P. M.

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**Guaiaicum Resin and Iodine Reaction.** By HAGER (Chem. Centr. 1872, 352).

DURING the examination of a Berlin bee-master's secret "*Wundersaft*," which proved to be a mixture of dilute sugar syrup with an ammoniacal tincture of guaiacum resin, the author tested for iodine by shaking with chloroform and ferric chloride. The chloroform had a deep violet colour, but on close examination was found free from iodine. This reaction gives a means of detecting guaiacum in a cloudy mixture. The colour of the chloroform disappears in a few hours.

C. H. G.



**New Process for Estimating the Iodine in Kelp Liquors, Mineral Waters, &c.** By E. SONSTADT (Chemical News, xxvi, 173).

THE addition of an alkaline permanganate to a liquid containing an iodide in solution, converts the iodide into iodate, if sufficient free alkali or alkaline carbonate be present to prevent liberation of iodine. A process based upon this reaction and devised by the author, has been found very serviceable.

Alkaline solutions of chlorides and bromides are not in the least acted upon by permanganate solution, nor do they, or any other salts ordinarily occurring with iodides, interfere with the transformation of the iodide into iodate. Organic matter does not interfere if the permanganate be added in sufficient excess. The process is as follows:—

Excess of potassium permanganate solution is added to the solution of salts containing iodide, until a slight permanent tint of the permanganate coloration remains. The solution is first made alkaline, best by the addition of sodium hydrate, to an extent adjusted to the proportion of iodide present; but always so as to preclude the possibility of the liberation of iodine. After filtering, a small quantity of a soluble sulphate is added, provided no sulphate be previously present, and then barium chloride solution in moderate excess. The precipitate washed on a filter, is next heated with potassium sulphate solution in excess. The filtrate contains the whole of the iodine originally present, as *potassium iodate*. The iodic acid may be estimated volumetrically by any of the usual processes, or the mixed iodate and sulphate may be ignited at a low red heat, and the potassium iodide estimated either volumetrically or gravimetrically.

The transformation of iodide into iodate as above, is complete, as are also the precipitation of the iodic acid by a barium salt in presence of a sulphate, and the decomposition of barium iodate by heating with potassium-sulphate solution in excess.

An experiment is cited showing the extreme delicacy of this process: "One part of calcium-iodate contained in a quarter-million parts of liquid sufficed to give measurable iodine reactions in the precipitate thrown down by barium chloride."

Experiments made as to the solubility of barium iodate in hot and boiling water (the same barium chloride solution being used as in the former determinations), yielded results which convinced the author that the complete precipitation of iodic acid in presence of sulphuric acid by a barium salt is due to surface attraction between barium sulphate formed in the liquid and nascent barium iodate.

W. S.

**Occurrence and Detection of Vanadium and Titanium in Trap-Rocks.** By R. APJOHN (Chem. News, xxvi, 183).

PROF. ENGELBACH, of Bonn, having mentioned to the author that he had found vanadium and titanium in the trap-rock occurring in the adjacent Rhine district, the latter thought it would be interesting to examine specimens of trap from other localities for these rare metals.

Three different basalts were examined, viz., one from a trap-dyke at Dunamoe, county Wicklow, one from the Giant's Causeway, and one from Vicentine, Italy.

*Detection of Vanadium.*—8 grams of finely powdered mineral were fused with four times the weight of sodium carbonate; a small quantity of nitre was added after cooling, and the crucible was again heated, not above a dull red heat. The mass was treated with water, and the aqueous solution boiled with ammonium carbonate, and filtered to remove silica. The filtrate evaporated with hydrochloric acid was treated with hydrogen sulphide and filtered. To the filtrate was added an equal volume of very concentrated ammonia solution, and hydrogen sulphide was passed through the liquid, till all the free ammonia was saturated. In the case of each specimen, the solution assumed a beautiful and intense cherry-red colour, a sure indication of the presence of vanadium. This coloured liquid was filtered off and saturated with hydrochloric acid; the precipitate containing sulphur and vanadium sulphide was dried and ignited, and the residue melted with a pinch of nitre. From the potassium vanadate thus formed, the characteristic blowpipe reactions were obtained.

*Detection and Estimation of Titanium.*—12 grams of the finely powdered rock were fluxed with six times their weight of acid potassium sulphate; the cooled mass was powdered and exhausted with cold water; and the aqueous solution, largely diluted, was boiled with acid sodium sulphite. When the precipitation was complete, and the liquid had cooled, a little sulphurous acid was added to redissolve iron and alumina. This precipitate of titanic acid was converted into potassium titanofluoride in the usual manner, and weighed. The titanofluoride was also dissolved in hot water, and the titanic acid precipitated by ammonia, ignited, and weighed. The results obtained were as follows:—

	Per cent. of titanic oxide ( $\text{TiO}_2$ ) in trap rock.
Wicklow trap .....	1.58
Giant's Causeway basalt.....	0.70
Vicentine basalt .....	0.91

The blowpipe reactions with the titanic acid obtained were perfectly characteristic. W. S.

### Estimation of Iron in Blast-Furnace Slags. (Chem. Centr., 1872, 304.)

It frequently happens that the iron chemically combined in blast-furnace slags is by no means insignificant in amount, and it therefore becomes interesting to know from time to time what that amount is.

It is, however, very difficult, and sometimes impossible, to decompose these slags by means of acids. This is particularly the case with crystalline slags, the vitreous slags being much more decomposable. A portion of finely pulverised vitreous slag, treated with hydrochloric acid, is dissolved, leaving a siliceous jelly, but the crystalline portion is scarcely affected. It is recommended that ammonium fluoride be

employed to decompose the slags, as it can be prepared and kept without difficulty.

The finely pulverised sample is heated in a platinum crucible on the water-bath, with three to four times its weight of ammonium fluoride. Sulphuric acid is gradually added, the heat being continued until all appearance of ebullition ceases. The crucible is then heated on the sand-bath, until the acid begins to volatilise. Cold water is now added, when everything must dissolve but the calcium sulphate. The precipitate is thrown on the filter and washed, till the wash-water no longer contains iron. The filtrate is treated with zinc in a retort, to reduce the iron, which is determined in the solution by means of potassium permanganate. W. S.

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**Detection of Bismuth by the Blowpipe in presence of Lead and Antimony.** By H. B. CORNWALL (Chem. News, xxvi, 150).

VON KOBELL observed that bismuth heated on coal, with a mixture of iodide of potassium and sulphur, produces a characteristic red coat. This reaction appeared to the author to be applicable to the detection of small quantities of bismuth in presence of lead and antimony. The iodide mixture, consisting of five parts sulphur and one part iodide of potassium, was heated in open tubes 4 inches long and not less than half an inch wide. The following results were obtained by heating the substances named with an equal weight of the mixture in the tube over a spirit lamp.

*Lead oxide.*—First, part of the sulphur sublimed and condensed above the assay, its heavy vapours also burning at the lower end of the tube. Then copious yellow fumes passed through the tube, and an abundant sublimate condensed, which commenced about one-third of an inch above the assay, and when *quite cold*, had a pure bright yellow colour.

*Lead oxide, with 1 per cent. of Bismuth trioxide.*—The same phenomena as above, but one-third of an inch above its lower edge the yellow sublimate was replaced by a broad and distinctly red ring of the bismuth sublimate.

*Lead oxide, with  $\frac{1}{4}$  per cent. of Bismuth trioxide.*—The same as in the last experiment, but the bismuth sublimate was orange-red, although so distinctly marked as to leave no doubt that even a smaller proportion of bismuth could have been detected.

*50 parts of Lead oxide, 50 parts of Antimony trioxide, and 1 part of Bismuth trioxide.*—The white antimonial sulphide entirely concealed the bismuth reaction. To obviate this, the mixture of the three oxides was mixed with an equal volume of sulphur, and treated with the blue flame for several minutes. The resulting fused sulphides were removed to a flat coal, and treated alternately with the oxidising and reducing flames, until the antimonial fumes had nearly ceased, and an impure blue lead flame appeared. The residue, powdered and treated as before in the open tube, yielded a distinct bismuth sublimate, about one-third of an inch above the lower edge of the yellow sublimate. The experiment was repeated with equal parts of the oxides of lead and antimony,



containing  $\frac{1}{2}$  per cent. and  $\frac{1}{4}$  per cent. teroxide of bismuth, and, as was to be expected, the bismuth reaction was more distinct than when the bismuth was present with lead only.

Care must be taken not to confound with the bismuth sublimate a sublimate of iodine, which may condense on the upper part of the tube, but at a greater distance from the assay.

J. B.

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**Detection of Gold in Sea-Water.** By E. SONSTADT (Chemical News, xxvi, 159).

EXPERIMENTS made on specimens of sea-water collected at various times at Ramsey Bay, Isle of Man, prove that gold exists therein, but as the quantity is certainly less than one grain in a ton, it is too small to admit of separation, or even detection, by the usual tests. Besides the difficulty of detection arising from the small quantity of gold present, there is another difficulty of a graver kind, due to a continuous re-solution of the gold after it has been separated in the metallic state. This re-solution is owing to the separation of iodine, under the influence of reducing agents upon the iodate of calcium, which the author has previously shown exists in sea water. Even if the reducing agent is added in large excess, oxidation takes place so rapidly under the continuous re-forming power of calcium iodate, that, sooner or later, according to the excess of reducing agent added, the stage arrives at which the iodine is set free, and the suspended gold is redissolved.

Of three entirely different methods employed, the following is one which may be performed upon so small a quantity of sea-water as 150 to 200 c.c. Two or three decigrams of pure ferrous sulphate are dissolved in the water, which is acidulated with two or three drops of hydrochloric acid. The solution is heated in a *chemically clean* and well-glazed porcelain dish, over a small flame, so managed that the flame may touch the under part of the dish, without causing ebullition. Under these circumstances a lustrous film of ferric oxide forms in the dish, commencing from the portion directly heated by the flame. The heat is continued without boiling, until the sea-water is evaporated to about half, or so long as the film increases in extent and in lustre. The liquid is then poured off, the strongly adherent film is rinsed with a little water, and then about 50 c.c. of strong chlorine-water is allowed to stand in the dish for an hour or two, after which it is slowly evaporated down (over the film) to a few drops, a drop of dilute hydrochloric acid being added towards the end of the evaporation. The liquid, which should be nearly colourless, is then poured into a test-glass, containing a few drops of solution of stannous chloride, when, after a few minutes, the liquid takes a bluish or purplish tint, which may be exactly matched by a drop or two of suitably diluted solution of gold added to a corresponding proportion of tin-salt in another glass. The formation of the film depends upon the iron being in a particular state of oxidation, and the best way is, after adding the ferrous sulphate and hydrochloric acid to the sea-water, to leave it exposed to the air for a few hours before heating the liquid to obtain the film. The chlorine solution off the sea-water films may be dried up in a porcelain crucible

with precipitated lead, and gold beads obtained by cupellation, after fusing the lead into a button with borax; but for this experiment at least half a litre of sea-water should be taken, and even then the bead obtained is too small to be weighed. Similar experiments in the same vessels, and with the same reagents, upon simple water, and on water containing chloride of sodium and alkaline sulphates, never yielded the slightest coloration with stannous chloride.

J. B.

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**Elliott's Method for the Estimation of Carbon in Bone Charcoal, Graphite, Anthracite, &c.** By F. A. CAIRNS (Chem. Centr., 1872, 277; Dingl. Polyt. J., ciii, 470).

THE author directs attention to a noteworthy point in this process which appears to have been overlooked by its inventor, viz., the weighing of the absorption tube at the conclusion of the experiment after cooling. The neglect of this point may cost the experimenter one- or two-tenths of a per cent. He also thinks it advisable to use an aspirator at the commencement of an experiment, in order to avoid a possible loss of carbon dioxide through the caoutchouc connectors, in consequence of the pressure resulting from a very rapid evolution of gas.

Elliott's method, in regard to its employment in the estimation of the total carbon in iron and steel, has already been proved accurate. The author has performed a number of experiments to test its accuracy with regard to graphite obtained from pig-iron, bone charcoal, anthracite, and bituminous coals, compared with that by burning in oxygen. The results obtained by this method (oxidation with chromic acid and sulphuric acid), and by combustion in oxygen, were found to agree very closely.

W. S.

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**New Methods of Analysing Ethers.** By J. A. WANKLYN (Chem. News, xxvi, 134).

ONE method is to take about 5 or 10 grams of the ether, and digest it with excess of aqueous solution of baryta in a sealed tube, until the decomposition of the ether is complete. The tube is then opened, and the amount of alcohol formed is estimated by its specific gravity. Professor Wanklyn showed some years ago that the acid obtained in saponifying an ether may be accurately titrated.

A second process proposed by Professor Wanklyn is to decompose the ethers with excess of strong hydriodic acid. This is specially designed for the fats, which are salts of glycerin, and ought to yield Erlenmeyer's iodide of isopropyl. By this means it is hoped that the percentage of glycerin derivable from any given fat may be estimated.

J. B.

**Process for the Volumetrical Estimation both of Copper and of Sugar.** By F. WEIL (Ann. Chim. Phys. [4], xxv, 109—121).

THIS method is based on the two facts, (1.) That in a hot solution containing excess of hydrochloric acid the least trace of cupric chloride gives a greenish colour, the tint being deeper as the quantity of acid is larger. (2.) Stannous chloride instantly reduces green cupric chloride to colourless cuprous chloride.

A solution of stannous chloride containing 6 grams of tin per litre is titrated with a solution of cupric sulphate containing 4 grams of copper per litre; 25 c.c. of this solution are treated with 10 c.c. of concentrated hydrochloric acid, and heated to boiling, and the tin solution is rapidly added till the liquid becomes colourless; 10 c.c. more acid are now added, and if the liquid acquires thereby a greenish tint, tin-solution is slowly dropped in till no colour remains. To make quite sure that the tin solution is in slight excess, 1 c.c. of the cooled liquor is treated with a drop of saturated solution of mercuric chloride; 0.05 c.c. of the tin-solution in 30 c.c. of liquid causes a distinct turbidity of calomel when thus treated. This volume is therefore deducted from the total volume of tin-solution used, and the strength calculated from the remainder.

*Estimation of Copper.*—1. *When Iron and Nickel are absent.*—The substance is heated with strong nitric acid; the nitric is expelled by sulphuric, or in the case of silver, by hydrochloric acid; the volume of the solution is brought to 250 c.c. or 500 c.c.; 25 c.c. are then treated with the tin-solution exactly as above described in the case of the standard copper-solution, and the quantity of copper present is calculated from the volume of liquid employed.

2. *When Iron is present.*—*Process A.* 25 c.c. of the solution to be tested are reduced as just described. A fresh quantity of the same volume is then heated with water, metallic zinc, and platinum-foil till all the iron is reduced. The copper, together with any lead, tin, or arsenic that may be present is thus precipitated as metal. The iron is then estimated in the decanted liquid with permanganate. The strength of the tin-solution having been calculated for iron from the number for copper, the proper deduction is made from the total quantity used. *Process B.* The metallic copper precipitated as described under *A* may be dissolved and directly estimated with tin-solution without estimating the iron. *Process C.* The solution containing ferrous salt, described in *A*, may be treated with permanganate till the latter is in distinct excess, then boiled till no red colour remains but that due to iron. Tin-solution is now added till the iron is reduced, and the quantity thus used is subtracted from the total quantity employed for copper and iron together.

3. *When Nickel or Cobalt is present.*—*Process A.* The solution of the substance in nitric acid or aqua regia is nearly neutralised with sodium carbonate and then agitated with barium carbonate till all the copper and iron are precipitated. The precipitate is dissolved in acid, and the copper in it is estimated by tin-solution. *Process B.* See above, 2, *B*.



Arsenic does not interfere with this method, since arsenic acid is not reduced by stannous or cuprous chloride. The results obtained vary only a few tenths of a per cent. from those obtained in the gravimetric way.

*Estimation of Sugar.*—Instead of adding the solution of sugar to Fehling's solution till the blue colour is only just visible, an excess of the latter is used, the cuprous oxide filtered off, the solution acidified, and the copper in it estimated with tin-solution. The quantity found is subtracted from the total quantity contained in the volume of Fehling's solution employed, and the remainder is that which has been used in oxidising the sugar.

B. J. G.

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**Experiments with Fehling's Copper Solution.** By T. L. PATTERSON (Bull. Soc. Chim. [2], xviii, 31, and Chemical News, xxv, 149).

THE author concludes from his experiments—(1.) That the glucose-destroying power of Fehling's solution varies directly (within certain limits) with the quantity of alkali present, but that when the amount of alkali reaches a certain point, all the copper cannot be precipitated. (2.) That old solutions (as is known) can be renewed by adding alkali to them, and may even be made of greater oxidising power than the original solution. (3.) That the solution is partly decomposed when exposed to light by absorption of oxygen; and (4.) still further by splitting up of the tartaric acid into other fixed acids, whereby the alkalinity is decreased. (5.) That the second only of these actions goes on in the dark, and that only to a small extent. (6.) That the solution is best preserved in dark-green glass bottles.

B. J. G.

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**On the Combination of Glucose with Copper, and on Trommer's Test.** By E. SALKOWSKI (Pflüger's Archiv. für Physiologie, vi, 220).

WHEN copper sulphate is somewhat carelessly added in Trommer's test, so that a precipitate falls and does not again dissolve, a colourless, slightly alkaline filtrate is occasionally obtained, which is free both from sugar and copper. The author gives the proportions required for complete precipitation. The precipitate after washing contains only cupric hydrate and glucose, which can readily be separated by hydrogen sulphide, and is free from all but minute traces of alkali. It may be dried in air with little or no decomposition. It is soluble in alkali, and its solution is reduced on heating.

When this is done, reduction is complete, and the supernatant liquid is free both from sugar and copper. As one molecule of sugar reduces 5 of copper, the precipitate must consist of sugar and copper in this proportion. Trommer's test consists of two parts, the formation of this compound and its solution in excess of alkali, which quickly decomposes

it. Uric acid is occasionally completely precipitated from the alkaline solution by copper sulphate.

T. L. B.

### Reaction of Cholesterin with Sulphuric Acid. By E.

SALKOWSKI (Pflüger's Archiv., vi, p. 207).

THE best way of testing this reaction is to dissolve a few centigrams of cholesterin in about 2 c.c. of chloroform, and then shake it with its own bulk of strong sulphuric acid. The chloroform quickly becomes blood-red, and then cherry-red or purple, a colour which it retains for several days. A few drops poured into a basin become blue, green, and then yellow. This change seems due to traces of moisture, and the original colour may be restored by sulphuric acid. The sulphuric acid under the chloroform presents a distinct green fluorescence. When dropped into glacial acetic acid, the liquid, in about half an hour, becomes violet, or, if much diluted, rose-coloured, with a green fluorescence, and exhibits such a resemblance to the liquid obtained by diluting Pettenkofer's test for bile-acids with glacial acetic acid, that it is often impossible to distinguish between them. The spectra they present are also very much alike, but the spectrum of each is somewhat variable. That of the cholesterin solution indicates that it consists of two substances, whose proportions vary. Water takes up from the chloroform solution a sulpho-acid, which forms crystallisable salts with barium. The reaction of cholesterin with sulphuric acid is slightly modified when only traces of cholesterin are present, and the author recommends as a test for it, that a few granules should be dissolved in 1 c.c. of chloroform, and gently warmed with an equal volume of sulphuric acid, occasionally shaking. The chloroform quickly acquires a rose or violet colour. The sulphuric acid becomes lemon-yellow, with a distinct green reflection. By dilution with glacial acetic acid, a liquid is obtained of a faint red colour, with green fluorescence.

T. L. B.

### Estimation of Uric Acid. By RICHARD MALY (Pflüger's Archiv. f. Physiol., vi, 201—206).

THE author finds, in opposition to Schwanert, that Salkowski's results (see page 333 of this volume) are perfectly correct, and that 0.0386 to 0.0468 gram of uric acid can be precipitated from 200 c.c. of urine by silver nitrate, after as much as possible has been previously thrown down by hydrochloric acid. Hofmann found only 0.011 to 0.014 gram in 200 c.c. of urine, but the urine on which he experimented deposited little or no uric acid on the addition of hydrochloric acid. Not less than 72.2 per cent. of the uric acid which is not precipitated by hydrochloric acid, can be recovered by the use of silver nitrate. He considers that the precipitate thrown down by silver nitrate is a double compound of silver urate with an alkaline or earthy urate. Silver urate seems to be incapable of existence alone. Uric acid and silver oxide are soluble in presence of much free ammonia, forming a clear solution if other salts are only present in small quantity. In presence

of salts of alkalis, or alkaline earths and free ammonia, uric acid forms double salts in various proportions with silver. These are white, gelatinous, flocculent, and very sparingly soluble, much more sparingly than free uric acid. They are especially adapted for the precipitation and recognition of minute quantities of uric acid, which are not precipitable by hydrochloric acid.

T. L. B.

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**Estimation of Potash in Urine by Tartaric Acid.** By E. SALKOWSKI (Pflüger's Archiv., vi, 209).

THE author finds that the amount of potash in urine cannot be exactly determined by weighing the precipitate produced by tartaric acid, as this precipitate contains varying quantities of ammonium tartrate and traces of sodium, and occasionally of phosphoric acid.

T. L. B.

---

**Estimation of Urea and Chlorides in Urine containing Potassium Iodide.** By E. SALKOWSKI (Pflüger's Archiv. f. Physiologie, vi, 214).

WHEN a solution of urea containing potassium iodide is titrated by Liebig's method, a yellow colour with sodium carbonate is observed long before all the urea is precipitated. In presence of sodium chloride, however, this is not the case, and the titration may be readily effected, provided the solution contains less than 3 parts of potassium iodide to 10 of urea. The final reaction occurs with seven-tenths of a c.c. of mercury-solution less than it would otherwise do. The urea in a urine and baryta mixture containing potassium iodide can also be readily estimated, but its presence makes the process somewhat more difficult and the final reaction occurs a little too soon, occasioning an error of about  $\frac{1}{10}$ th per cent. If exact results are desired, it is advisable first to precipitate the urine with silver-solution, as recommended by Hoppe and Neubauer. The estimation of chlorides in such urine is also somewhat inexact. The best method of avoiding error is to evaporate 10 c.c. of urine with potassium nitrate, incinerate, dissolve in water, acidulate with sulphuric acid, and remove the iodine by agitation with carbon bisulphide. If the nitrous acid formed during fusion is not sufficient to liberate all the iodine, a little red nitric acid or potassium nitrite is to be added. The aqueous solution is neutralised with sodium carbonate, evaporated, and lastly titrated with silver solution. The results are generally a little too low, but are quite serviceable. If great exactness is not required, and the quantity of potassium iodide is small, it may be neglected.

T. L. B.

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**Detection of Iodine in the State of Potassium Iodide in Urine.**

By DR. PELLOGGIO (Gazzetta Chimica Italiana, ii, 75—78); also by C. GIANNETTI (*ibid.*, 253—257).

IN 1870 Dr. Pelloggio published a new method of detecting iodine in the state of potassium iodide, namely, by subjecting the liquid under



examination to the action of an electric current, after addition of starch-paste and slight acidulation with sulphuric or hydrochloric acid. This method was applied to the detection of iodine in urine by Campani, who found it to be inferior in delicacy to the method of testing with bromine-water with addition of starch or of carbon bisulphide (see last volume of this Journal, p. 1084).

Pelloggio, in the paper above referred to, describes experiments on the detection of iodine, both in normal urine to which potassium iodide had been added, and in the urine of patients to whom potassium iodide had been administered, from which he draws the following conclusions:—

1. That for the detection of iodine in urine, the method with carbon bisulphide and bromine-water is not so delicate as that with bromine-water and starch. Moreover, the former method is not to be depended upon, because it is next to impossible to hit the exact quantity of bromine-water required to develop the red coloration without again destroying it; and lastly, it is incapable of detecting very minute quantities of iodine in urine.

2. That the method with bromine-water and starch, though more delicate than that with carbon bisulphide, is inferior to that which consists in the use of starch-paste, hydrochloric acid, and the electric current.

- 5 cubic centimeters of urine containing 0.05 gram of potassium iodide having been diluted with somewhat more than a five-fold quantity of water, and the liquid being divided into two equal portions, one portion treated with starch-paste and a drop of bromine-water did not give any blue coloration, whereas the other portion mixed with starch-paste and hydrochloric acid and electrolysed, exhibited a number of slender filaments of iodide of starch.

3. That these reactions are less delicate in iodised urine than in the pure solution of potassium iodide, because the urine contains a substance, namely urea, which interferes with them. Hence the colour disappears on agitation, but reappears on further addition of bromine-water.

The superior delicacy exhibited, according to Pelloggio, by the electrolytic method, is attributed by him to the circumstance that the current likewise acts on the urea in such a manner as to prevent its action on the iodide of starch.

A still more delicate test for iodine in presence of urea is, however, afforded by nitromuriatic acid and starch-paste, the nitromuriatic acid decomposing the urea with formation of nitrous products, and at the same time furnishing the chlorine required to decompose the potassium iodide. With this reagent a distinct blue colour is produced with three drops of iodised urine containing 0.00016 grm. of potassium iodide, and dissolved in 12 cub. cent. of water (Pelloggio).

The relative delicacy of these tests has also been examined by Giannetti, who has arrived at results opposite to those of Pelloggio. Operating on 5 cubic centimeters of urine containing 0.05 gram of potassium iodide, and diluted with various quantities of water, he obtains the results given in the following table:—

Experiments.	Ratio of urine to water.	Urinous liquid used in each experiment.	Potassium iodide contained in each sample.	Reactions.	
				With starch-paste and bromine-water.	With carbon bisulphide and bromine-water.
1. Normal urine..... 50 c.c. Potassium iodide... 0·05 gm.	..	5 c.c.	gram. ·005	Very deep.	Very deep.
2. Urine of the first } experiment..... } 5 c.c.					
Distilled water ..... 25 c.c.	1 : 5	5 c.c.	·0008333	Deep.	Deep.
3. Urine of the second } experiment..... } 5 c.c.					
Distilled water ..... 5 c.c.	1 : 11	5 c.c.	·00041666	Very plain.	Deep.
4. Urine of the third } experiment..... } 5 c.c.					
Distilled water ..... 5 c.c.	1 : 23	5 c.c.	·00020833	Plain.	Very plain.
5. Urine of the fourth } experiment..... } 5 c.c.					
Distilled water ..... 5 c.c.	1 : 47	5 c.c.	·00010416	Weak colour.	Plain.
6. Urine of the fifth } experiment..... } 5 c.c.					
Distilled water ..... 5 c.c.	1 : 95	5 c.c.	·00005208	Nothing.	{ Very perceptible rose colour.

From these experiments it appears that the reaction with bromine-water, with addition either of starch-paste or of carbon bisulphide, is more delicate than the electrolytic method, inasmuch as it gives distinct colorations with the iodised urine, diluted in the one case with 47, and in the other with 95 volumes of water, whereas, according to Pelloggio's statement, the limit of the electrolytic reaction appears to be reached when urine containing the same proportion of potassium iodide is diluted with somewhat more than five times its bulk of water. Moreover, the reaction with bromine and bisulphide of carbon appears to be the most delicate of all.

The following are the conditions most favourable to success in these experiments:—The undiluted urine (5 c.c.) containing the potassium iodide in the proportion above-mentioned, requires eight drops of saturated bromine-water to produce the red coloration with carbon bisulphide, and six drops to produce the blue colour with starch-paste; a somewhat larger quantity deepens the colour, a large excess destroys it. By diluting the urine more and more, a point is at length reached (Experiments 5 and 6) when a single drop of the bromine-water is too much, and destroys the reaction; but by diluting the bromine with four or five times its volume of water, and adding the liquid drop by drop, the reaction soon shows itself. Strong agitation interferes with the reactions, especially when the proportion of potassium iodide is small; but by gentle agitation fine colorations are obtained; this indeed is an essential condition for obtaining a delicate reaction with bromine and bisulphide of carbon.

When the experiment is made with undiluted urine, a considerable quantity of bromine-water is required to obtain the reaction, either with starch-paste or with carbon bisulphide. This fact was observed by Pelloggio, who attributed it to the presence of urea (see above). Giannetti also finds that urea destroys the colour of iodide of starch, but that urine destroys the colour of this compound more quickly than it would be destroyed by the corresponding quantity of pure urea in aqueous solution. Stale urine gradually loses the power of decolorising the iodide of starch. The colour produced by bromine with sulphide of carbon is also destroyed by pure urea and by fresh urine, but not quite so quickly as that of iodide of starch.

Lastly, Giannetti has compared Pelloggio's reaction with nitromuriatic and starch-paste with that obtained by the use of bromine-water and carbon bisulphide, and still finds that the latter is the most delicate test hitherto proposed for the detection of iodides in urine.

H. W.

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**Estimation of Nitrobenzene in Bitter Almond Oil.** By  
E. BOURGOIN (Bull. Soc. Chim. [2], xviii, 113).

THE method given at page 843 of this volume is adapted only for a qualitative examination, but the following process furnishes 90 per cent. of the nitrobenzene in a fit state for weighing. 5—10 grams of the essence are agitated in a wide-mouthed flask, with 20—40 c.c. of concentrated solution of acid sodium sulphite, and then treated with ether. The solution is filtered quickly, evaporated to dryness, and the residue of nitrobenzene is weighed.

B. J. G.

---

**New Method of Detecting Fuchsine.** By G. ROMEI (Gazzetta Chimica Italiana, ii, 81).

CASALI's method, which consists in adding ammonia to wine, or other liquid supposed to contain fuchsine, and taking up the rosaniline with ether, is not applicable when but a small quantity of the colouring matter is present. One-tenth of a milligram in 100 c.c. may be detected by agitating the suspected liquid with its own volume of amylic alcohol, when the latter will be tinted a beautiful red if fuchsine be present. In the case of wine, the natural colouring matter must first be precipitated with basic lead acetate.

B. J. G.

---

**Behaviour of Alkaloids towards Sugar and Sulphuric Acid.**  
By R. SCHNEIDER (Pogg. Ann., cxlvii, 128—132).

*Morphine* is at once coloured a beautiful purple-red, when a small quantity of a mixture of the base (or its salts) with 6 or 8 parts of sugar is treated with concentrated sulphuric acid. No browning of the sugar is observed. The colour lasts for  $\frac{1}{4}$ — $\frac{1}{2}$  hour, then gradually becomes blue, violet, dirty blue-green, and lastly dirty yellow. This series of colours can be rapidly produced by adding a little water. 0.00001 gram can



be clearly indicated by this reaction. Dilute solutions of morphine are to have about as much sugar added as will dissolve in them, and then to be brought in contact with sulphuric acid, when a beautiful rose-red zone will develop itself where the two liquids meet.

*Codeine* closely resembles *morphine*, except that the reaction succeeds best when the sulphuric acid is not the most concentrated. *Codeine* is distinguished from *morphine* by being readily taken up by chloroform from an alkaline solution.

*Aconitine*, for which there are no good chemical tests, is coloured a beautiful rose-red, soon becoming dirty violet and brown. The *aconitine* is to be stirred with a drop of sulphuric acid, and then a drop of concentrated sugar-solution brought in contact with it. There is a certain degree of resemblance between the reactions of *aconitine* and those of *morphine* and *codeine*. It is distinguished, however, from them by Dragendorff's process for separating the alkaloids; *codeine* and *aconitine* are taken up by benzene from an alkaline solution, but not *morphine*; *aconitine* is quite insoluble in water; *codeine* dissolves easily, especially in hot water.

*Delphinine*, intimately mixed with a drop of sugar-solution on a porcelain plate, gives also a characteristic reaction, when a small drop of sulphuric acid is dropped into the middle of it. The acid becomes yellow, then yellowish-brown with a dirty green border, and on addition of a small drop of water, assumes a magnificent green colour, which soon passes into a dirty green, and then into brown.

The behaviour of *narcotine*, *narceine*, *cinchona-bases*, *strychnine*, *brucine*, *atropine*, *colchicine*, *emetine*, and *picrotoxine* is not characteristic.

E. D.

### New Quinimetric Process. By P. CARLES (Bull. Soc. Chim. [2], xviii, 98—100).

THE following quinimetric process is found to be accurate, simple, and rapid, and superior, therefore, to any hitherto recommended.

An average sample of the bark is powdered and sifted; 20 grams of it are mixed with 6 or 8 of slaked lime in 35 of water; the mixture is dried at a gentle heat, and transferred to a percolator; chloroform (about 150 grams) is added in successive portions till the bark is exhausted; the last portions of chloroform are displaced by water; the chloroform is then evaporated, and the mixture of alkaloids and cereo-resinoids is treated with dilute sulphuric acid (1 in 10); the acid solution is passed through a very small filter, then brought to the temperature of ebullition, and rendered only faintly acid in reaction by the addition of ammonia-water. In consequence of its complete insolubility in solution of ammonia sulphate, the sulphate of quinine is thus completely precipitated, and forms when cold a white crystalline cake. It is drained on a small filter, its mother-liquor is displaced by a few drops of water, and it is then pressed, dried, and weighed. It is better to dry it thoroughly at 100°, and allow afterwards 12 per cent. for the water of crystallisation thus lost. The other alkaloids remain in solution; they can be precipitated, weighed, and identified by the action upon them of washed ether.

Test experiments made upon artificial mixtures of the alkaloids gave very satisfactory results, with the exception that they showed that when the cinchonine exceeds the quinine in quantity, some of it may be precipitated along with the quinine, so that the sulphate of quinine must in this case be recrystallised.

E. D.

*On Opium Extract and the Examination of Opium.* By E. HEINTZ (Arch. Pharm. [2], cl, 36; Chem. Centr., 1872, 489).

**On Ziegler's Method of Albumin Estimation.** By DE CONINCK (Chem. Centr., 1872, 381).

ZIEGLER'S method of estimating the values of different varieties of albumin consists in dissolving 20 grams of the substance to be examined in 0.1 litre of water, straining through a sieve, taking up 10 c.c. of clear liquid, and coagulating by a boiling 20 per cent. alum solution; the appearance and volume of the coagulum are noted, and then it is washed, dried, and weighed.

De Coninck finds that the process yields albumin containing not more than 1 per cent. of alumina, and is sufficiently accurate for the purposes of the calico-printer, although it does not yield the total contents of albumin. The presence of gum hinders the precipitation of the albumin, but that of dextrin does not: thus the author found the following numbers:—

Albumin alone.	80 parts albumin, 20 „ gum.	70 parts albumin, 30 „ gum.	60 parts albumin, 40 „ gum.
Albumin found, 1.58	1.10	0.90	0.60
Ditto taken, 1.58	1.26	1.11	0.95

Albumin alone.	Albumin 50. Dextrin 10.	Albumin 80. Dextrin 20.	Albumin 60. Dextrin 40.	Albumin 50. Dextrin 50.	Albumin 40. Dextrin 60.
Albumin found, } 1.35.....	1.21	1.07	0.90	0.75	0.32
Albumin taken, } 1.35.....	1.22	1.08	0.80	0.68	0.41

C. R. A. W.

## Technical Chemistry.

**Separation of Sulphur from Sulphuretted Hydrogen.** By W. WELDON (Dingl. Polyt. J., ccv, 74).

THE sulphuretted hydrogen is allowed to act on iron and manganese oxides suspended in water, air is then let in; and this treatment is re-

peated until a considerable amount of sulphur is obtained, which is then separated.

The soda waste of the soda-manufacturer, decomposed by means of carbonic acid, furnishes the sulphuretted hydrogen, sodium carbonate being at the same time formed.

M. M. P. M.

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**The Use of Calcium Sulphite in Breweries.** By VICTOR GRIESSMAYER (Dingl. Polyt. J., ccv, 77).

THE calcium sulphite is prepared by passing sulphur dioxide gas into water, in which powdered marble is suspended, until a clear solution is obtained.

If the casks have a small quantity of this solution (1 part to 1000 parts of beer), poured into them before the beer is put in, all souring is prevented; and even if the souring has set in, it is stopped, unless it has gone too far, by this solution.

M. M. P. M.

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**New Process for the Manufacture of Potassium Iodide from the Mother-liquors of Kelp.** By E. SONSTADT (Chem. News, xxvi, 183).

THIS process consists in converting the alkaline iodides contained in the mother-liquors from kelp into iodates, first precipitating all sulphuric acid from the liquors by barium solution, in which process all the silica is also thrown down, together with other impurities. The filtered mother-liquor is then boiled down and fused to destroy organic matter. The fused mass dissolved in water is rendered alkaline by addition of caustic or carbonated alkali, in the proportion of 5 molecules of caustic alkali and 10 molecules of carbonate for each atom of iodide contained, for all but the last of the under-mentioned processes.

The iodic acid is precipitated by a soluble barium salt, and the precipitate heated with solution of potassium sulphate, which gives potassium iodate in solution. This solution is dried down, the residue is fused, and the fused potassium iodide thus obtained is dissolved and crystallised.

For the conversion of iodide into iodate the following processes are employed:—

(1.) Chlorine is passed through the liquid till all the iodide is transformed into iodate, but no longer.

(2.) Solution of a permanganate is added until a slight permanent red coloration remains. The liquid is separated from the manganese precipitate, and the latter may be furnaced with soda and nitre to recover the permanganate.

(3.) An electric current is passed through the dilute solution, the electricity being most economically obtained from electro-magnetic machines worked by water power.

(4.) The purified mother-liquor is evaporated to dryness, with addition of an atom of an alkaline chlorate for each atom of iodate present. The mixture is then cautiously heated below redness until the iodine is converted into iodate.



After separating the iodic acid, the bromide remaining in the mother-liquor may be converted into bromate by either of the processes (1) or (4), and potassium bromide obtained by the same methods as used for obtaining potassium iodide.

Processes (2) and (3) are not applicable to the formation of bromate.

W. S.

**The Chili Saltpetre and Iodine Industry of Tarapaca.** By R. WAGNER (Dingl. Polyt. J., ccv, 75—76).

IN a district of about a square mile there are eleven establishments, producing together 6150 centners of saltpetre per day. (A centner = about 1 cwt.).

The establishment nearest to Iquique is about 30 English miles distant from that port, and is about 3,000 feet above the sea level. A railway is being constructed to connect the saltpetre districts with Iquique.

The percentages of sodium nitrate in the raw mineral vary from 77.9 to 36.8, and sodium chloride from 32.02 to 12.90.

In 1 litre of the mother-liquors the amounts of iodine vary from 4.8 to 2.3 grams.

M. M. P. M.

**Contribution to the History of Glass Manufacture.** By E. SIEGWART (Dingl. Polyt. J., ccv, 39—55).

THE first part of this paper is historical. The author then shows, by analyses of a number of specimens of window glass, that the composition of the best glass for this purpose is expressed by the formula,  $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 6\text{SiO}_2$ . In such a glass the proportion of silica to lime and soda is as 1 : 0.325. In good glass, this proportion may vary from that just stated to 1 : 0.365; but even with the proper proportion of constituents, if great care be not taken in regulating the heat of the glass oven, an inferior glass will be formed.

The author investigates the action of the atmosphere and rain on glass, and the changes produced in it when it has remained for some time under ground. His results have been already forestalled by others.

When the panes of window-glass are being made smooth, one side of them is exposed to a higher temperature than the other; on this—the upper surface—the sulphuric acid (which is generally present) acts, sulphates of the alkalis being produced, which are partially washed away by the water used in cleaning the glass. A plate of window-glass placed in a moist room soon became covered on its upper surface with a crystalline incrustation, no such incrustation being visible on the under surface, that is, on the part less exposed to the heat of the oven when the plate was rolled out.

A plate of glass which tends to become thus incrustated by atmospheric influences will be rendered dim and opaque by a half-hour's exposure to a mixture of 16 parts calcium fluoride, 120 parts water, and 1.5 part

sulphuric acid of 66° Baumé. In the latter part of his paper the author examines the results of the investigations of Pelouze, Dumas, &c., concerning devitrified glass.

M. M. P. M.

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**On Superphosphate.** By A. MILLOT (Bull. Soc. Chim. [2], xviii, 13—21).

ARDENNES coprolites, when treated with rather more sulphuric acid than is necessary to convert the tribasic into monobasic phosphate, harden into a compact mass. They have not, therefore, been much used, unless when mixed with some other phosphate. Millot finds, however, that this hardening does not take place when for 100 Ardennes coprolite, 60 of sulphuric and 15 of hydrochloric acid are used.

If a phosphate has not been finely ground, a portion of the calcium carbonate is left unacted upon. By the time such manure is dry, this carbonate reacts with the free phosphoric acid, and dicalcic phosphate is formed. This change is one cause of "reduction" or retrogradation. The author concludes from his experiments—(1.) That "reduction" also takes place when tribasic phosphate is left unacted upon by the acid: the reduction ceases when the drying of the manure in the air is terminated, and may be prevented by keeping it moist. (2.) During drying, the ferrous oxide is transformed into ferric oxide, and combines with the free phosphoric acid, this being another cause of the formation of reduced phosphate. (3.) The portion insoluble in water, after drying, if excess of sulphuric acid has been used, is a mixture of ferric and dicalcic phosphate. (4.) If all the tricalcic phosphate has been attacked the first day, the only reduction that then takes place, if the temperature is kept below 40°, is due to iron.

B. J. G.

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**Arsenic from Alkali Works.** By H. A. SMITH (Chemical News, xxvi, 176).

SOME time ago the author published the results of several analyses of the amounts of arsenic contained in different species of pyrites, and in several of the products in the manufacture of which the acid was employed. He carried his analyses as far as the carbonate of soda, in which no arsenic was found. He now endeavours to show that the arsenic also escapes into the air.

When the salt used for the production of hydrochloric acid is treated with sulphuric acid containing arsenic, this becomes converted into the trichloride. This compound is said to be completely decomposed by contact with water, so that after passing along with hydrochloric acid gas through the condensing towers, it would scarcely be expected that any traces of the arsenic originally present would be found in the escaping gas.

This is, however, the case, a certain quantity of the arsenic trichloride escaping the action of the water in the condensing towers, and passing along with a very small proportion of the hydrochloric acid gas to the chimney.

A deposit found in the flue leading from the salt-cake furnace to the condensing towers, the coke contained in the towers themselves, the gas in the flue leading to the chimney, and the smoke escaping to the chimney were all analysed, and found to contain arsenic.

	Arsenic trioxide, per cent.
Flue deposit, mean of 9 determinations .....	43.434
Coke from condensing towers, mean of 3 determinations	2.986

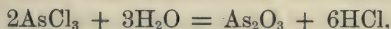
Air in the flue passing from flue to chimney, rate 31.722 cubic feet per hour, mean of 12 determinations.

	Arsenic trioxide, grains.
Per 1,000 cubic feet .....	0.158
Per hour .....	5.012
Per day .....	115.134

Air taken about 10 feet from bottom of chimney.

	grain.
Mean of 9 determinations per 1,000 cubic feet ..	0.086

The arsenic probably escapes either as arsenious acid, or as arsenic trichloride; if as the latter, it is ultimately transformed into the former, thus:—



W. S.

### Electrotype. By Prof. HEEREN (Dingl. Polyt. J., cciv, 487).

THE employment of graphite with gypsum and gutta-percha moulds causes much trouble and loss of time, because the graphite must be rubbed till it assumes a metallic lustre, which, though a matter of no great difficulty with smooth even surfaces, is very troublesome when irregularities occur. Better results are obtained when the gypsum mould, soaked in wax, is thickly covered over with a mixture of silver nitrate solution supersaturated with ammonia and alcohol, and the mould exposed to the action of sulphuretted hydrogen, whereby sulphide of silver is formed, which is a good conductor. The free ammonia in the solution causes it to adhere more readily to the wax, leaving on drying a uniform, unbroken covering of the silver compound.

When a somewhat powerful current from 4 or 5 Daniell's elements is used, the layer of copper quickly diffuses itself over the whole surface, whereas by employing a feebler current, a softer and less friable copper is obtained.

A good method of preparing the solution is as follows:—

1 gram of lunar caustic is dissolved in 2 grams of water,  $2\frac{1}{2}$  grams of ammonia of sp. gr. 0.960 are added, and then 3 grams of absolute alcohol.

V. S.



**Pyro-gilding as compared with Water-gilding.** By J. BAYNES THOMPSON (Chemical News, xxvi, 137).

WATER-GILDING by means of gold amalgam is not only unhealthy for the manipulator, but is applicable only to metals that will amalgamate, and therefore cannot be applied to iron and steel. Pyro-gilding is the only method applicable to iron and steel, and even for other metals it is superior to water-gilding in cheapness and healthiness, and to other methods in results. The process is as follows:—After the article has been thoroughly cleaned, the first coating of gold is put on, which to all appearance is a perfect coating, but when it has passed through the furnace, if the article be of steel or iron, the gold has disappeared into the steel, &c., which appears just slightly tinged with yellow. The process is repeated a second and third time, when the coating comes out of the furnace as brilliant as when it went in, and this is the test that the gilding is complete. For gilding, nothing further is required but a good hard burnishing, but for any special purpose, as many more coatings may be put on as may be deemed necessary.

J. B.

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**Plating with Aluminium.** By CLEMENS WINKLER (Chem. Centr., 1872, 347).

AFTER a long preface, the author says that plating with aluminium cannot be effected either by electro-deposition or by rolling out a metal to which a sheet of aluminium has been soldered. The brittleness of the alloys of aluminium is the preventing cause in the second case.

C. H. G.

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**Estimation of the Temperature of the Combustion-zone of the Blast-furnace.** (Chem. Centr., 1872, 351.)

A CRITICISM directed to show that the estimations of temperature in the blast-furnace as made by Bell, Tünner, Akermann, &c., are not decisive, since these observers left out of account, or were unable to measure, many features which are required for an accurate determination. Among other points, there is instanced the heat required to decompose the water vapour of the blast, the uncertainty as to the proportions of carbonic acid and carbonic oxide in any given section; the heat required for the reduction of silicium, &c., &c.

C. H. G.

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**Danks's Puddling Furnace.** By P. TÜNNER (Chem. Centr., 1872, 327).

By the rotary puddling furnace there is not only a quicker, more complete, and cheaper puddling effected than in the hand-worked furnace, but a more complete separation of the phosphorus is brought about. The more complete separation of the phosphorus depends upon the fact that pure rich iron ores are used for fettling the furnace. To

every 600 pounds of pig, 650 to 670 pounds of puddled iron are added, and 80 to 100 pounds of iron at least are reduced from the ore which forms the furnace lining. According to Danks's statement, about 50 per cent. of the iron contained in these pure fettling ores should be obtained. From the above it follows that for every charge made, about 100 pounds of iron from the ores is carried away in the slag, and since the ores contain, or should contain, but little silica, and the pig can contribute but a small quantity, this slag is very basic, and rich in iron. Its composition is undoubtedly much altered by the many further additions of squeezer and puddle-slag; but the furnace lining, with which the iron during every agitation is being brought into contact, continually offers a prevailing oxidising surface of ferric oxide. The separated phosphorus can pass into the slag only as phosphoric acid, reducing a portion of ferric oxide, and combining with another portion of ferrous oxide. It has long been known that the passing of the phosphorus into the slags occurs only in the case of those very rich in iron. In any other form of the process it would be difficult, or at all events too costly, to use oxide of iron in such quantity and of such a degree of purity to separate the silica and phosphorus, as is done in the case of Danks's puddling-furnace lining. As it is, these impurities may indeed be looked upon as useful, since they contribute to the increased yield of puddled iron.

W. S.

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**Dephosphorizing Puddling Process for the Preparation of good Bar Iron from Phosphorized Pig.** By TH. SCHEERER (Dingl. Polyt. J., cciv, 482).

THE chemical agents employed in this process are calcium chloride and sodium chloride. These two chlorides are fused together in about equal proportions, and the fused mass constitutes the dephosphorizing mixture. Calcium chloride alone would not be sufficiently active, and sodium chloride would be too volatile to produce any effect. The presence of other metallic chlorides, as, for instance, manganese, iron, and magnesium chlorides, must be avoided. In order thoroughly to mix this dephosphorizing charge with the metal in the furnace, the former is gradually introduced, wrapped up in waterproof paper cases each containing about 2 lbs., and the whole is well stirred up. The ordinary puddling process requires no other alteration, but it is greatly shortened by the powerful dephosphorizing action of this mixture.

It is practically found necessary to employ three times as much of the mixture as there is phosphorus present in the pig iron. Thus, for a pig iron containing  $2\frac{1}{2}$  per cent. of phosphorus, in a charge of  $3\frac{1}{2}$  cwts.,  $2\frac{1}{2} \times 3\frac{1}{2} \times 3 = 26\frac{1}{4}$  lbs. of the mixture would be required. The minimum amount requisite has to be experimentally determined for each kind of pig.

W. S.

**Manufacture of Russian Iron Plates.** (Chem. Centr., 1872, 335.)

THE iron for this purpose is refined from pig obtained from magnetic iron ore, or red and brown hæmatites, by the use of wood charcoal and cold air. The conversion of the pig into wrought iron is effected with wood charcoal either in the refining fire or the puddling furnace. The iron must be more granular than fibrous, and must contain sufficient carbon.

The apparatus for working consists of one or two pairs of rollers, and two kinds of hammer. The plates are again heated in ovens of special construction. The rollers should make fifty revolutions per minute. The hammers are of wrought-iron faced with steel. Each anvil consists of a block of white cast-iron. The iron plates are subjected to a process of alternately heating to redness and rolling, and finally, after heating again, they are well hammered.

W. S.

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**Silicium and Manganese in Steel and Bar Iron.** By W. MRÁZEK (Chem. Centr., 1872, 360).

IN working bar iron and steel, considerable quantities of carbon may be present, without much damage when the temperature is raised only to a red heat, if manganese be also present. At a white heat the bad effects of much carbon or silicium become more apparent, and it is here also that the influence of a large proportion of manganese is visible. The peculiar characteristics of steel and bar iron are less altered by admixture of silicium or carbon than of sulphur or phosphorus. Carbon is, however, more hurtful than silicium. The improvement which the presence of manganese brings about in these irons may, the author says, depend on the power of the manganese to combine with the silicium, and thus to increase the relative quantity of free metallic iron; it increases also the power of the iron for resisting heat, because the melting point of manganese silicide is higher than that of silicide of iron.

M. M. P. M.

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**Effect of certain Methods of Boiling in the Vacuum-pan of a Sugar Factory.** By F. JICINSKY (Dingl. Polyt. J., cciv, 503—508).

SHOWS by experiment that boiling to a fine even grain results in a larger turn-out of sugar than either boiling "blank" or to a very large grain.

C. H. G.

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**Bye-products of the Manufacture of Starch and Sugar.** By J. FITTBOGEN (Ann. d. Landwirthschaf; Wochenblatt, 1872, 290).

THE residue from the manufacture of potato-starch was fluid, and of a feeble acid reaction; it contained 94.8 per cent. of water. The dry



substance contained in 100 parts,—albuminoids 6·84, starch 60·66, dextrin 5·22, glucose ·29, fat ·51, crude fibre 8·11, non-nitrogenous matter undetermined 15·26, and ash 3·11. The ash was quite similar in composition to that of the potato.

The residue left in the neutralization vat belonging to the manufacture of sugar from starch contained, when dry, about 70 per cent. of inorganic matter, chiefly calcium carbonate and sulphate, with about 10 per cent. of tricalcic phosphate, the residue of the bone-black used.

R. W.

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**Adaptation of the Solubility of Cellulose in Ammoniacal Copper Solution to the Preparation of Waterproof Paper, Roofing Tiles, Artificial Wooden Slabs, &c. (Dingl. Polyt. J., civ, 514).**

If linen rags or wood saw-dust be fully dissolved in ammoniacal copper solution, and the solution then allowed to evaporate to dryness, a semi-transparent, brittle glass is left, for which no use has yet been discovered. But if the action of the solvent be prevented from effecting more than a commencing superficial solution, in which the fibres maintain their original form and disposition, remarkable results are obtained. A sheet of paper, left only an instant in the ammoniacal copper solution, and then passed between rollers and dried, becomes quite impervious to water, and does not lose its power of cohesion at the boiling heat. Two sheets of paper thus treated adhere firmly together, and form one piece. By treating a large number of sheets of paper in the same manner, artificial boards are obtained. Linen pieces thus treated furnish a very elastic material of great cohesive strength. Linen and paper may also be treated together, and a material is obtained said to surpass every kind of wood in point of firmness and strength.

Extremely serviceable roofing tiles may be thus made, resisting all irregularities of wind and weather. Pipes for conveying water and gas, articles of clothing, and even boats, can be constructed with this material.

W. S.

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**The Sensibility of Collodion as affected by the Varying Proportion of Pyroxylin and Iodizing Salts. By E. ZETTNOW (Chem. Centr., 1872, 361—362).**

THE author made a number of experiments with carefully prepared collodion, from which it would appear that with the same amount of pyroxylin a certain addition of iodizing salts increases the sensibility of the collodion, but beyond this it rather diminishes this sensibility. The limit is  $1\frac{1}{2}$  per cent. of a solution containing 20 per cent. iodine and bromine, in the proportion of 3 parts iodine to 1 part bromine, added to collodion containing  $\frac{1}{4}$ ,  $\frac{1}{2}$ , or  $\frac{3}{4}$  per cent. pyroxylin.

The collodions should not contain less than about  $\frac{1}{2}$  per cent. of pyroxylin, nor should less than  $1-1\frac{1}{2}$  per cent. iodine-solution, or more than about 2 per cent. be added.

The raw collodion should be made as thick as possible, and iodised so that the product shall contain  $1\frac{1}{2}$  to  $1\frac{3}{4}$  per cent. iodine and bromine.

M. M. P. M.

**Photographic Process with Silver Bromide Collodion.** By Col. STUART WORTLEY (Chem. Centr., 1872, 328).

THE emulsion for covering the plate is prepared with 480 parts crude collodion, 7 parts anhydrous cadmium bromide, 30 parts uranium nitrate, and 18 parts silver nitrate. To purify the uranium salt, a portion is dissolved in 2 parts of ether, and the solution allowed to stand two hours, when the water of crystallisation is found collected at the bottom of the flask. For the preparation of the emulsion, the ethereal supernatant liquid is taken. If the solution is not acid, one or two drops of nitric acid are added to every 30 grams. It is important that a good collodion wool be employed, some kinds giving a collodion which is useless for this emulsion. A strongly alkaline developing solution is used; the uranium salt assists the developing solution energetically, and acts very favourably in this respect. The work-room must be lighted by a decidedly orange-coloured light, that used in the wet process being insufficient in the emulsion process.

For developing, the following solution is made:—To 1 ounce of water and alcohol are added 20 drops of pyrogallic acid solution, 40 to 60 drops of solution of ammonium carbonate, and 5 to 10 drops of solution of potassium bromide; all these solutions are prepared in the proportion of 1 : 5. The ammonium carbonate must be fresh, and not effloresced, and the pyrogallic acid of best quality.

The emulsion is poured on the plate, and, after solidifying, the layer formed is washed with water, and exposed to the light in the wet condition. The developing solution is immediately poured on, whereupon the picture quickly appears, and is strengthened by addition of more ammonia. Further strengthening is effected by repeated application of the developing solution. The negatives are complete in every respect.

W. S.

**Illuminating Gas from Bohemian Lignite.** By BODENBENDER (Ann. der Landwirth., Wochenblatt, 1872, 348).

A GAS with an illuminating power equal to that of gas made from English coal and paraffin oil, is made at Sudenburg-Magdeburg, from Bohemian lignite, with a saving of from 25 to 33 per cent. in price. The addition of  $\frac{1}{4}$  to  $\frac{1}{3}$  lb. weight of coal to the lignite improves the coke, and does not injure the gas.

E. K.

**New Method for the Preparation of Alizarin from Parannaphthalene, Anthracene, or their Homologues.** By C. GIRARD (Bull. de la Soc. Ind. de Mulhouse, xlii, 54; Dingl. Polyt. J., cciv, 490).

THE product is employed which distils between  $290^{\circ}$  and  $360^{\circ}$ , and after being purified by distillation and pressure, the substance which

passes over between 300° and 335° is collected. This mixture is treated with potassium chlorate and hydrochloric acid, so that it is converted into tetrachlorinated products. These tetrachlorinated substances are oxidised either by nitric acid in the water-bath, or by a metallic oxide (red or brown oxides of lead), and sulphuric or acetic acids. In the first case, a mixture of dichlor-anthraquinone and chloride of chloroxyanthranil was obtained. These substances were treated in presence of a metallic oxide (zinc or cupric oxide, or litharge), with an alcoholic solution of sodium acetate. The metallic oxide removes the last atom of chlorine from the sodium chloroxyanthranilate, and converts it like the dichloranthraquinone into alizarin.

The purification is effected by means of benzol, petroleum, &c., which dissolve out the foreign matters, and by successive precipitations from the alkaline solutions by mineral acids. The foreign matters may also be separated by means of a little alum, when it is necessary to work with neutral potash or soda salts.

W. S.

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**Anthraflavic Acid.** By BRANDT (Dingl. Polyt. J., cciv, 513).

HITHERTO the yellowish shade of red, which is obtained with certain artificial alizarins of commerce, has been attributed to the presence therein of a yellow substance, which comes from the anthracene, and has been called anthraflavic acid.

A quantity of anthraflavic acid was procured from Messrs. Gessert Brothers, of Elberfeld, and after a series of experiments, it was found that this body (mono-oxyanthraquinone of Liebermann, anthraflavic acid of Schünck) possesses no colouring power at all. It not only does not colour alumina and iron mordants, but does not turn the alizarin-alumina lake yellow. On the contrary, it communicates a bluish tinge to the red, and makes the shade appear muddy.

Additions of anthraflavic acid were made in the case of reds from artificial alizarin, and from madder extract, when invariably it was found that the shades so obtained were less beautiful and less intense, and that they were tinged bluish.

The conclusion arrived at is that the yellow tinge, obtained with reds from "artificial alizarin for red," is due to a modification of the alizarin itself. This modification can be obtained by various treatments, but it is not anthraflavic acid.

W. S.

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**Colouring of Tinfoil.** (Dingl. Polyt. J., cciv, 512.)

VARNISHED tinfoil is much used, especially by confectioners and others, for wrapping up their wares.

Springmühl's coloured resin-solutions (aniline lakes) for colouring tin-foil, did not succeed as was expected, as they did not form a uniform coating, and were too frail to withstand the bending and folding of the tinfoil. On small surfaces the aniline lake gives a splendid coating, which is sufficiently durable if the tinfoil be used to cover, and not to wrap up.



The oldest, most serviceable, and with some modifications the simplest method, has this disadvantage, that the coating is soluble in water. Isinglass used to be employed as the fixing material, but soon gave place to the white gelatin of commerce. The tinfoil is laid on a flat glass plate, and fastened down with water, so that every part adheres evenly to the glass. It is then carefully smoothed out with a smooth stone, and the coloured gelatin solution is poured on. The glass plate is then gently inclined in all directions, to effect a uniform distribution of the solution, and the whole is rather quickly dried. The gelatin solution is made by dissolving a quantity of clear gelatin in distilled water, with the aid of heat, then adding the solution of the colouring matter to the required shade. The aqueous extracts of vegetable and animal colours used to be employed.

Springmühl confined himself entirely to aniline colours soluble in water, and obtained remarkably good results with both gelatin and isinglass. Of gum-arabic and gelatin the latter was found cheapest, most durable, and best. Collodion gives an exceedingly uniform, and tolerably elastic coating, which, if too thick, does not adhere well, and can be removed as a thin skin. A solution of collodion as dilute as possible must therefore be used. The tinfoil is warmed a little, the *coloured collodion* solution is poured over it, and the ether is allowed to evaporate spontaneously. If a thin layer of gelatin be first spread over, and then the collodion be poured on, the coating of the latter will adhere all the more firmly. Several other methods described by Springmühl for colouring tinfoil gave very unsatisfactory results.

W. S.

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**Nicholson- or Alkali-blue on Wool.** (Dingl. Polyt. J., cciv, 513.)

THE Nicholson-blue differs from all other aniline colours in this respect that whereas all others, such as fuchsine, aniline blue and violet, &c., are salts of an insoluble base, this alkali-blue possesses a base soluble in water, which in combination with acids, forms an insoluble deep-coloured salt. This base is colourless or rather only faintly-coloured. It is necessary therefore in order to obtain an actual colour, to combine the base already fixed in the fibre of the fabric with an acid, and this is accomplished practically by passing the already once treated wool into an acid-bath. A quantity of alkali-blue solution in water is treated with a borax, soda, or potash solution, and the woollen fabric is worked up in the filtered liquid, this being slowly heated almost to boiling. The piece is then rinsed in water, and then passed into a warm acid-bath (sulphuric acid), when the beautiful blue colour is developed.

This colour is said to be the most durable of all the aniline-blues.

W. S.

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**Dyeing Cotton Fabrics with Aniline Black.** By JUL. PERSOZ (Bull. Soc. Ind. de Mulhouse, xlii, 47; Dingl. Polyt. J., cciv, 491—496).

ALTHOUGH it has long been known that by the action of potassium bichromate upon certain aniline salts in concentrated solution, very

powerful oxidation takes place, resulting in the production of a rich black precipitate, and certain chemists have long endeavoured to make this fact practically available in dyeing cottons, they have not hitherto been successful. Thus, in endeavouring to dye a piece of stuff in a solution of bichromate and an aniline salt, if this solution was very dilute the black could not be obtained at all, and if concentrated, it was very soon precipitated in the bath. The solution was then cooled down to nearly  $0^{\circ}$ , when another evil made its appearance; for when the solutions were sufficiently concentrated for the production of the colour, chromate of aniline crystallised out on cooling. These crystals getting into the cloth produced spots, and when the influence of the low temperature was removed, there was danger of the piece taking fire in the neighbourhood of these spots, where a mutual reaction of the elements of the chromate was accompanied by considerable rise in temperature.

All the above difficulties the author overcame in the following simple way. The solutions, either successively or at the same time, were cast in the form of a fine spray upon the tightly stretched cloth by means of a horizontal brush to which a reciprocating motion was communicated in the vertical direction. By this means, although the reaction took place very rapidly, the production of the black could not possibly occur before the solutions were intimately mixed upon the fabric, and the latter was well soaked with the mixture.

It was now necessary to determine the following points, viz. :—

1. What aniline salts are most advantageous for the production of a beautiful black?

2. With what degree of concentration and acidity must they be employed?

The acetate must not be used, as no black is obtainable with it, neither can other salts with organic acids be used, viz., the tartrate, oxalate, or citrate, which are either but little favourable to the production of the colour, or are dear. The salts best adapted for the purpose are the sulphate, hydrochloride, and nitrate.

It was also found that if a too neutral solution were employed, the colour was developed either with great difficulty or not at all. With too great acidity on the contrary, the black was so rapidly formed that the two solutions had not time to mix sufficiently and to penetrate the pores of the cloth; and if a certain degree of warmth were employed, there was danger of burning the fibre.

After trying a number of comparative experiments with the hydrochloric, sulphuric and nitric acid salts, in which the proportion of acid employed to form the neutral salts was increased in the proportion 1, 2, and 3, the following conclusions were arrived at :—

1stly. The employment of neutral aniline salts must be avoided.

2ndly. The bi-acid aniline salts, especially the bisulphate, give good results. Of the hydrochlorides, the tri-acid salt is the best.

3rdly. The sulphates give a reddish black, whilst the hydrochlorides and nitrates give a black with violet or blue lustre.

4thly. A mixture of equal volumes of bi-sulphate and bi-hydrochloride of aniline gives excellent results.

5thly. It is necessary to use the potassium bichromate as a tolerably

concentrated solution. That used by the author contained not less than 80 grms. of salt to the litre. It is immaterial whether the bichromate be used before or after the aniline salt.

The method recommended above, gives first a dark green, which passes into pure black, when the cloth is washed in water and then passed through a hot soap-bath.

By printing the cloth with resins or fats, previous to dyeing, white patterns on a black ground may be obtained.

W. S.

**Removal of Ink-spots from Coloured Fabrics.** (Chem. Centr., 1872, 512.)

For fabrics which do not admit of the use of oxalic acid, chloride of lime, &c., a strong solution of sodium pyrophosphate is recommended; it is rather slow in its action, and old stains resist it for a long time, but with recent spots it is always successful.

H. W.

**Chalks for Marking Cloth, &c.** By MASSE (Dingl. Polyt. J., ccv, 77).

THESE chalks—which are of various colours, and are very useful to tailors, &c., as the marks made by them on cloth are distinct, and are easily brushed off without disfiguring the cloth—are made by rubbing up with pipeclay softened by water, ultramarine, ochre, &c., according to the colour desired, fusing this mixture in moulds, and drying it in a slightly heated room.

M. M. P. M.

**Preservation of Beer for Transport by Sea by Velten's Warming Process.** By O. KNAB (Dingl. Polyt. J., cciv, 339—342).

THE value of this process was put to the following experimental test:—Six champagne bottles were filled with the same beer, so that 4.5 centimeters were left in the necks for the corks and air-space. In each bottle was inserted an air-manometer, divided into 100 parts, so that the course of the fermentation might be measured by the amount of pressure exerted. Three of the bottles thus filled, and closed quite airtight, were marked  $A_1$ ,  $A_2$ ,  $A_3$ , and then placed in the water-bath, kept at the constant temperature of  $48^\circ$ , and allowed to remain a half hour. When this temperature was attained, the manometers indicated the following pressures:— $A_1 = 67$ ,  $A_2 = 66.5$ ; from  $A_3$  the cork was ejected, and on re-corking, some air was enclosed, resulting in the formation of acetic acid in small quantity (see analyses). The bottles had nearly three atmospheres' pressure to withstand. The three bottles  $B_1$ ,  $B_2$ , and  $B_3$  were placed in a warm room where the temperature in the day was  $20^\circ$  and at night  $15^\circ$ . The bottles remained from April 1st to the 18th, when the cork of  $B_1$  was ejected;  $A_1$ ,  $A_3$ , and  $B_2$  till the 25th May;  $A_2$  and  $B_3$  till the 30th June, during which period the manometer was



daily observed. It was found that the heated beer did not begin to ferment till about the fifteenth day, when a slow fermentation set in, which gradually increased, whereas the beer which had not been heated began to show decided signs of fermentation on the third day.

Analyses of the beer at the end of the periods gave the following numbers:—

		Alcohol.	Extrac- tive.	Sugar.	Dextrin.	Acetic acid.	Lactic acid.
I.	{ A <sub>1</sub> , 25th May, 1871...	3·7840	6·945	1·447	3·6729	—	0·360
	{ B <sub>1</sub> , " " " ....	4·4800	6·645	1·205	3·7323	—	0·540
II.	{ A <sub>2</sub> , 30th June, 1871 ...	3·9120	6·833	1·323	3·9114	—	0·1604
	{ B <sub>2</sub> , " " " ....	3·9405	6·304	1·108	2·7994	0·072	0·504
	{ B <sub>1</sub> , 18th April, 1871 ...	4·068	6·823	1·330	3·9564	—	0·2664
	{ A <sub>3</sub> , 25th May, 1871...	3·689	7·024	1·548	3·9169	0·012	0·288
	{ C.....	4·276	6·536	1·107	3·5721	—	0·162

C is a sample of beer which had lain bottled in the cellar. The formation of acetic acid is evidently due to the admission of air, and indicates the importance of perfect air-tight closing in preserving beer. The smaller quantity of alcohol and lactic acid, and larger quantity of sugar and dextrin contained in A than in B, testify to the efficacy of this warming process. The taste of the samples A was also exceedingly favourable to the process, being undistinguishable from samples which were taken from the cellar, and had been kept in ice.

The contents of the bottles marked B were tasted, and found flat and decidedly inferior to the former. When the beer is heated, the carbon dioxide is liberated under pressure, and on cooling, the beer remains flat, whilst the carbon dioxide remains under considerable pressure in the necks of the bottles. Fermentation again setting in, the more rapidly the warmer the situation, the beer gradually becomes again impregnated and regains life.

W. S.

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*Metallurgy of Manganese.* By HUGO TAMM (Chemical News, xxvi, 111).

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*Dermoy's Puddle Process* (Chem. Centr., 1872, 510).

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*Evil Effects of the use of Arsenic in certain Green Colours.* By F. W. DRAPER (Chem. News, xxvi, 29, 40, 52, 90, 102).

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*Use of Aniline Colours dissolved in Collodion.* By F. SPRINGMÜHL (Chem. Centr., 1872, 511).

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*Note on the Stability of Colours fixed on Stuffs in general and on Silk in particular.* By M. CHEVREUL (Compt. rend., lxxv, 744).

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*On Dyes and Dye-stuffs other than Aniline.* By F. C. CALVERT (Chemical News, xxv, 7, 19, 31, 41, 54, 65, 89, 114).

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*Notes on Pepsin and Bismuth, and Elixir of Pepsin and Bismuth.* By E. SCHEFFER (Pharm. J. Trans. [3], iii, 161).

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*Processes for distinguishing and separating Silk, Wool, and Vegetable Fibres in Mixed Tissues.* By E. KOPP (Chemical News, xxv, 100).

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*Use of Dynamite for Blasting.* By GOBIN (Dingl. Polyt. J., civ, 69; Annales des Mines, 1872, i, 65).

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*On Bessemer Steel and Crucible-cast Steel (Tiegel Guss-stahl).* (Dingl. Polyt. J., ccv, 113—118.)

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*Contributions to the Technology of Tannins.* By R. WAGNER (Dingl. Polyt. J., ccv, 137—144).

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*Endeavours to establish the art of Tanning on a Scientific Foundation.* By A. REIMER (Dingl. Polyt. J., ccv, 143—169; 248—267; 358—382; 457—484).

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